12

Illustrated World of Science Encyclopedia

Chemistry III:
ORGANIC AND
LAB EQUIPMENT

THE WORLD OF SCIENCE

VOLUME
12
CHEMISTRY III
Organic Chemistry and Lab Equipment

with

The Illustrated Science Dictionary

CREATIVE WORLD PUBLICATIONS, INC.
CHICAGO

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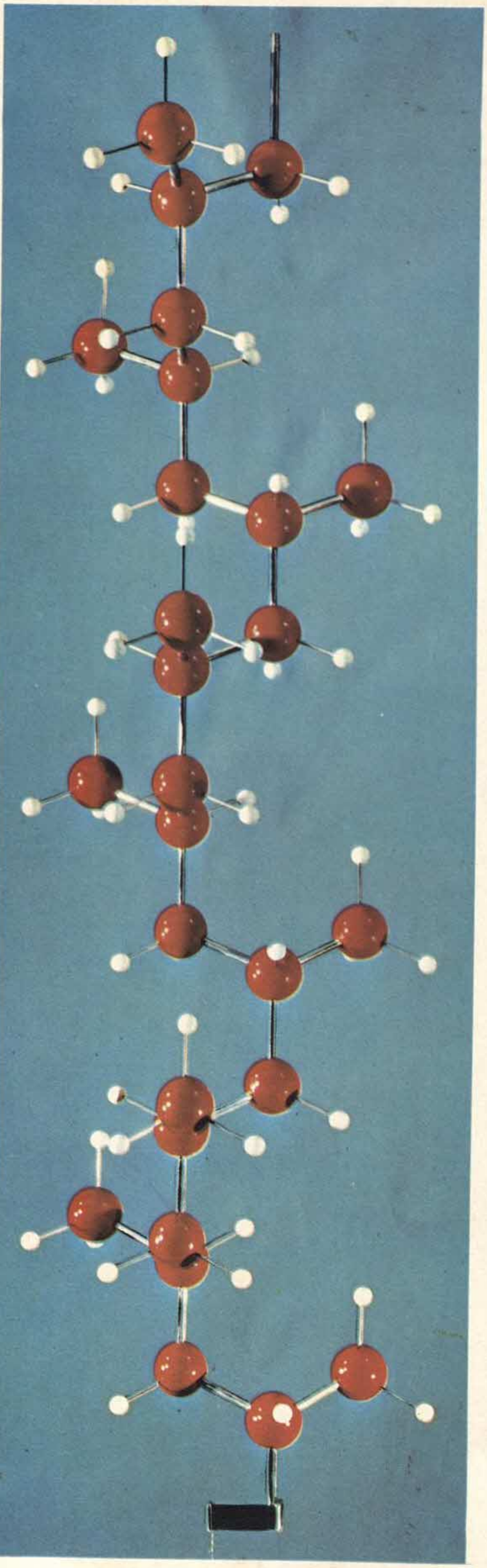

VOLUME 12

CHEMISTRY III

Organic Chemistry

INTRODUCTION

The element carbon has the unique ability to form stable chemical bonds not only with other elements of the periodic table but also with itself. Thus a large variety of molecules composed substantially of carbon (in combination with other elements such as hydrogen, oxygen, nitrogen, sulfur, and phosphorus—and the halogens—fluorine, chlorine, bromine, and iodine) occur naturally or can be synthesized.

The chemistry of carbon-containing molecules is called organic chemistry because early scientific thought held that these compounds could be derived only from plant and animal organisms but never by direct laboratory synthesis, as inorganic compounds could. This vitalism theory was disproved early in the nineteenth century when urea, a component of urine, was synthesized by accident from ammonium cyanate, an inorganic compound, simply by heating.

As time progressed, organic chemists devoted their efforts to the isolation and purification of new chemicals from natural sources such as coal, petroleum oil, and plant and animal extracts. These chemists were also concerned about the structures of these substances. After the atomic weight scale had been recognized and efficient analytical methods for determining the percentages of elements present in molecules had been developed, the molecular formula of compounds could be deduced. However, the arrangement of atoms in molecules could not even be guessed at until the German chemist Friedrich August Kekulé von Stradonitz hypothesized that carbon atoms always formed four chemical bonds while oxygen formed two bonds and hydrogen just one. Subsequently, the Dutch physical chemist Jacobus van't Hoff postulated that the four bonds of a carbon atom pointed to the corners of a regular tetrahedron. Thus, the three-dimensional arrangement of atoms in molecules assumed importance.

The ability of carbon to bond to itself, and the three-dimensional nature of atomic arrangements make possible incredible varieties of organic molecules. To date, a few million of these have been isolated or synthesized. These range from extremely simple molecules such as those found in natural gas to extremely large polymer molecules such as polyethylene, a well-known plastic, which still contains only carbon and hydrogen atoms albeit in large numbers. With the addition of other elements, organic molecules can become quite complex.

This volume begins with discussions of the equipment and approaches utilized in the isolation, purification, and synthesis of organic molecules. Then, various types of organic compounds and chemical principles are discussed. Central to an understanding of organic chemistry are concepts such as homology, functional groups, isomerism, stereochemistry, acidity and basicity, and oxidation and reduction.

Many different organic compounds having the same functional groups—that is, groups of atoms with particular arrangements and bonding characteristics—often react similarly. Thus organic chemistry can be organized according to the functional groups present within molecules. Molecules with the same functional groups but with different numbers of carbons are often called homologues. Different molecules having the same number of carbons, hydrogens, oxygens, and so forth, are called isomers. The three-dimensional aspects of structures and reactions are generalized by the term stereochemistry. Finally, many organic reactions can be classed as either acid-base reactions or oxidations and reductions; it is by these reactions that some functional groups are interconverted.

It is important to keep in mind that the complexities of organic chemistry, which have reached their zenith with the structures and reactions of enzymes and nucleic acids, are best appreciated through an understanding of simple organic compounds and their reactions.

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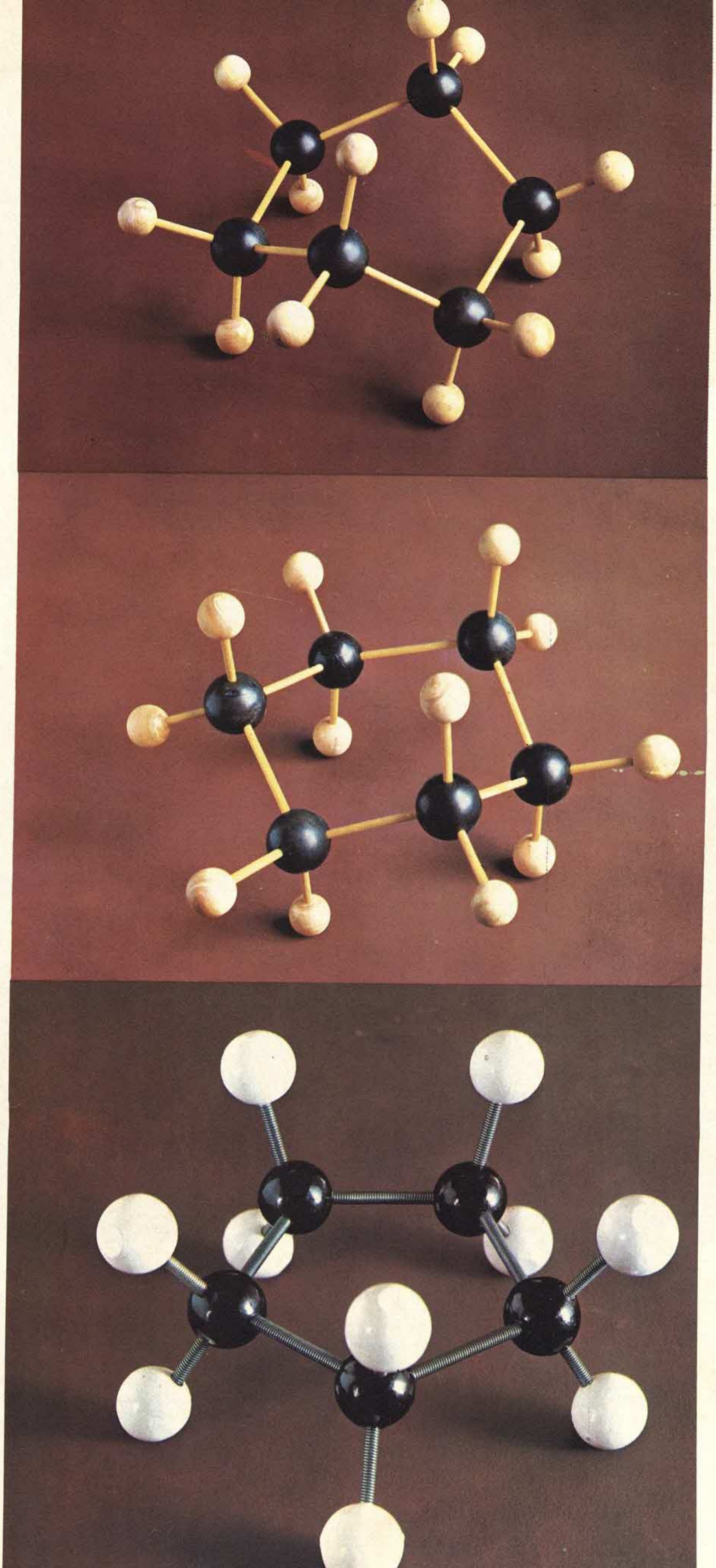


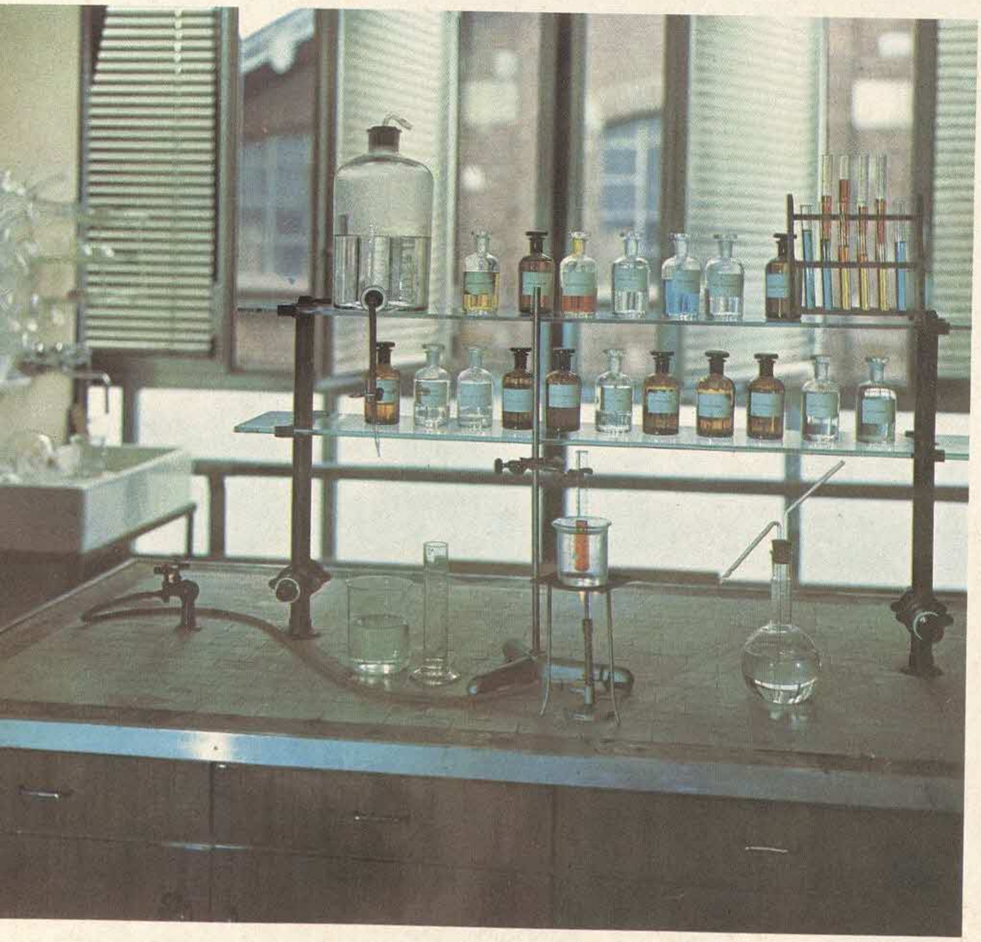
THE CHEMISTRY LABORATORY

alembics and test tubes

Today's chemistry laboratory is a far cry from the dark recesses in which medieval alchemists fruitlessly attempted the transmutation of lead into gold. A modern laboratory cannot even be considered a place for the all-inclusive study of chemistry. Because of the techniques and equipment required, no single laboratory can be expected to cope with the demands of all the various branches of chemistry: inorganic, organic, physical, nuclear, or medical, the last possibly incorporating elements from all the branches of chemistry.

Nevertheless, certain apparatus is more or less common to all laboratories, is required for basic operations, and can be obtained commercially at relatively low cost. Before setting up an analytical laboratory, however, certain guidelines must be considered. Not the least of these is a suitable location with adequate power and water. Furthermore, before any experimentation is attempted, a thorough knowledge of the subject matter is a prerequisite. The amateur should never initiate an experiment without total awareness of reagent and product characteristics, for insufficient preparation may end in disaster.

1a



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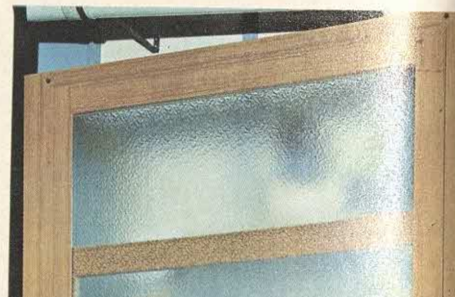
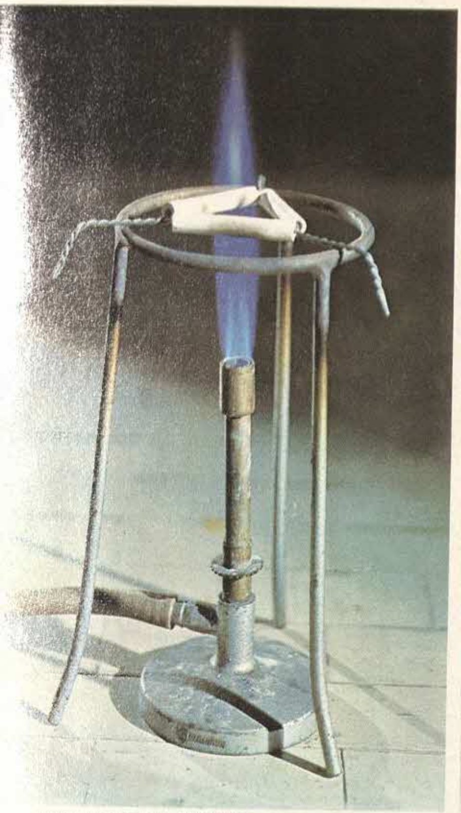


THE LABORATORY BENCH AND VENT— When experiments are to be performed in which dangerous or toxic materials are not produced, almost any room may be used as a laboratory. Otherwise it is absolutely necessary to work in a room equipped with a suitable bench and a venting system.

The laboratory bench shown in Illustration 1a has a top of chemical-resistant stoneware tiles. The disadvantage here is the spaces between the tiles that provide traps for spilled materials. Ideally, a seamless top of stainless steel or solid marble provides an easily cleaned surface. However, a common wood counter covered with a sheet of thick plastic will provide a corrosion-resistant surface, though with little resistance to heat. The room should be as spacious as possible, and have adequate ventilation provided by at least one window located near the bench.

If experiments will produce toxic fumes and gases, there should be provision for venting the laboratory. A well-equipped room should have a venting hood like the corner type shown in 1b, or have a hood directly over the bench. An adequate system can be made using a small window fan, making certain that it is firmly mounted, and connecting it to a flexible tube of fairly large diameter. It is necessary for the tube to reach the bench so that the tube can be held over the container in which the chemical reaction takes place.

2a



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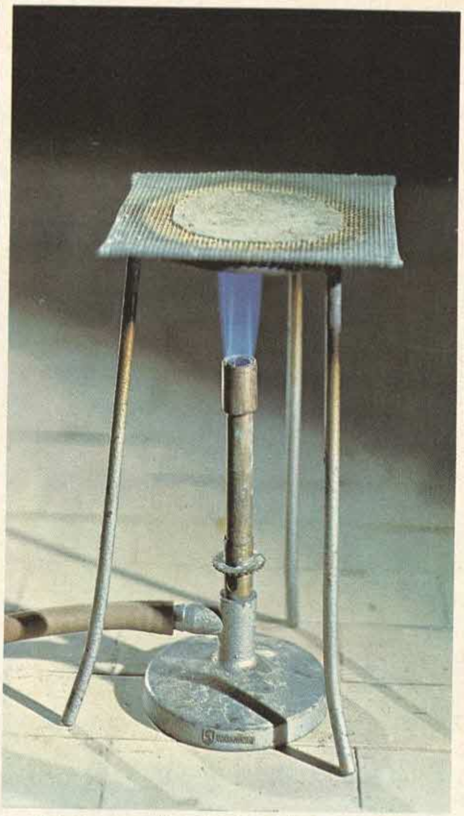
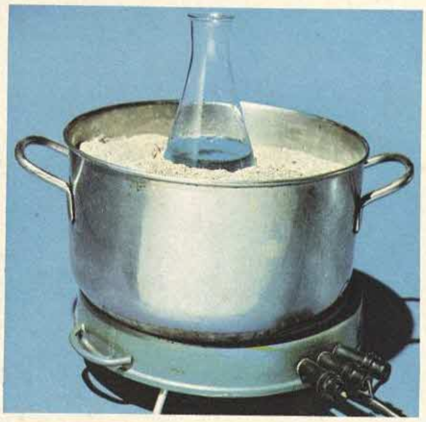


THE BUNSEN FLAME—One of the most important pieces of equipment in the laboratory is the Bunsen burner with an attendant gas source. Illustration 2a shows the burner and a clay triangle supported on a tripod. The triangle is used to hold crucibles in which substances can be fused, dried, or otherwise heated strongly. The same tripod supports a heat-spreading asbestos disk (Illustration 2b). This setup is used to heat glass containers away from direct contact with the flame.

SAND BATH—When materials are to be heated by an indirect method to temperatures in excess of 100° C, a sand bath can be used. A notable disadvantage here is the nonuniformity of heat, making accurate temperature control impossible. However, a high-temperature thermometer immersed in the material being heated does provide some degree of control.

4



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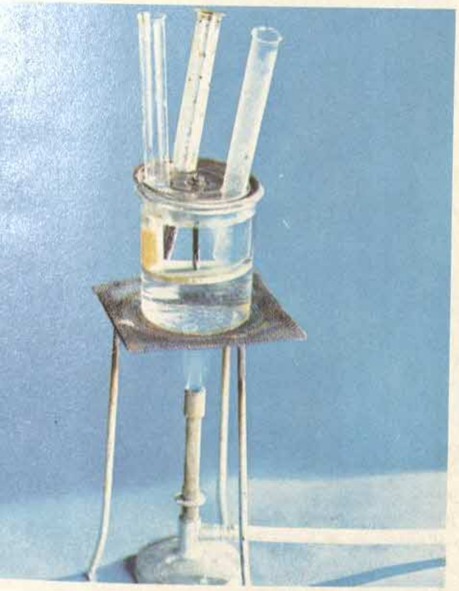
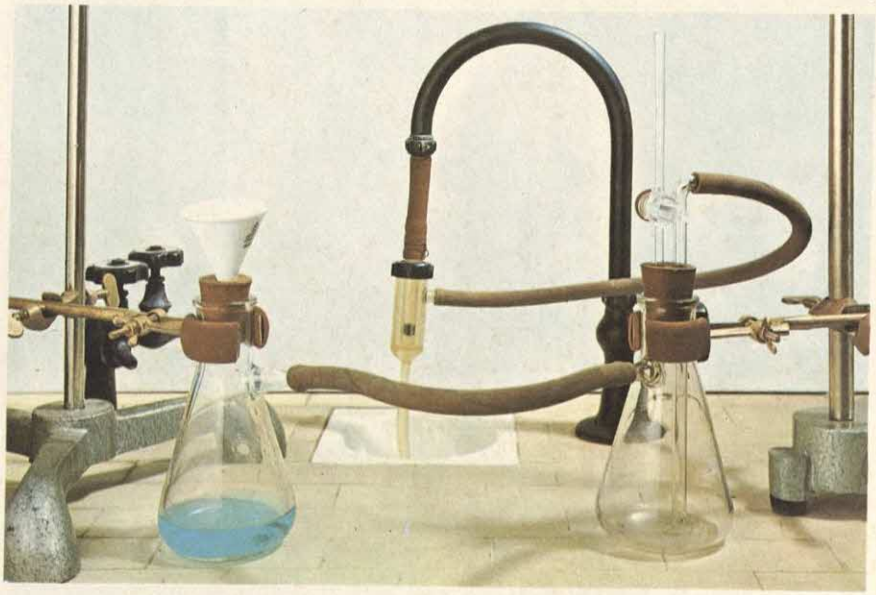


A WATER BATH—When it would be unwise to expose materials to a direct flame or to excessive heat, this indirect method is commonly used. The temperature of the bath will hold at the boiling point. The tubes in this illustration are supported in the beaker to prevent their being bounced around.

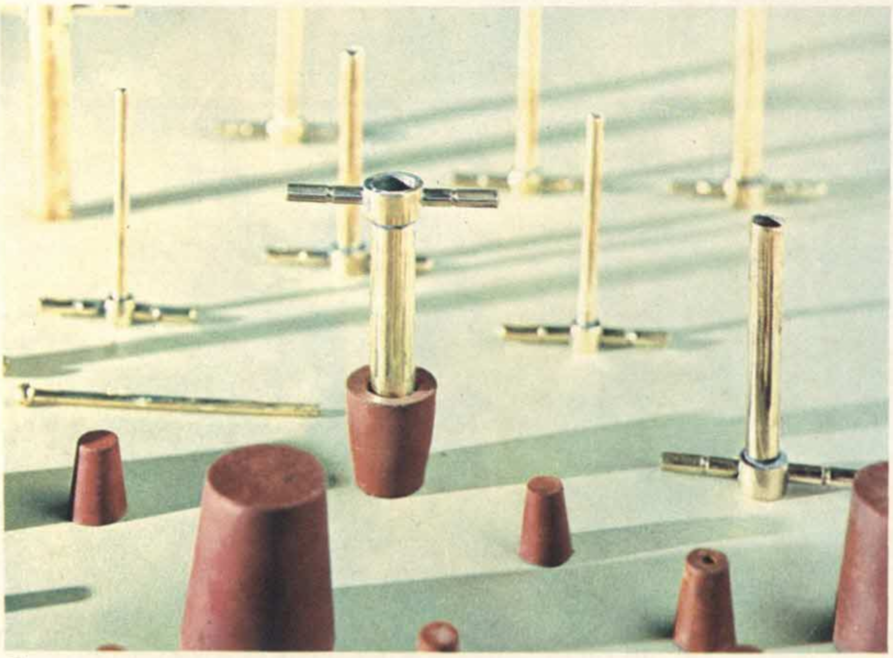
5



VACUUM FILTRATION—Certain filtration operations can be hastened by using a vacuum apparatus. That shown in this illustration produces the vacuum by the force of water flowing from the tap through a one-way valve into the sink. The two flasks are commercially available "aspirators," and the valve is easily obtainable through chemical supply houses.

RUBBER STOPPERS AND BORERS—Almost without exception, the well-equipped laboratory maintains a large supply of rubber stoppers in various sizes. Although stoppers can be supplied with predrilled holes, it is a good idea to have a set of cork borers available to drill solid stoppers for special application.

6



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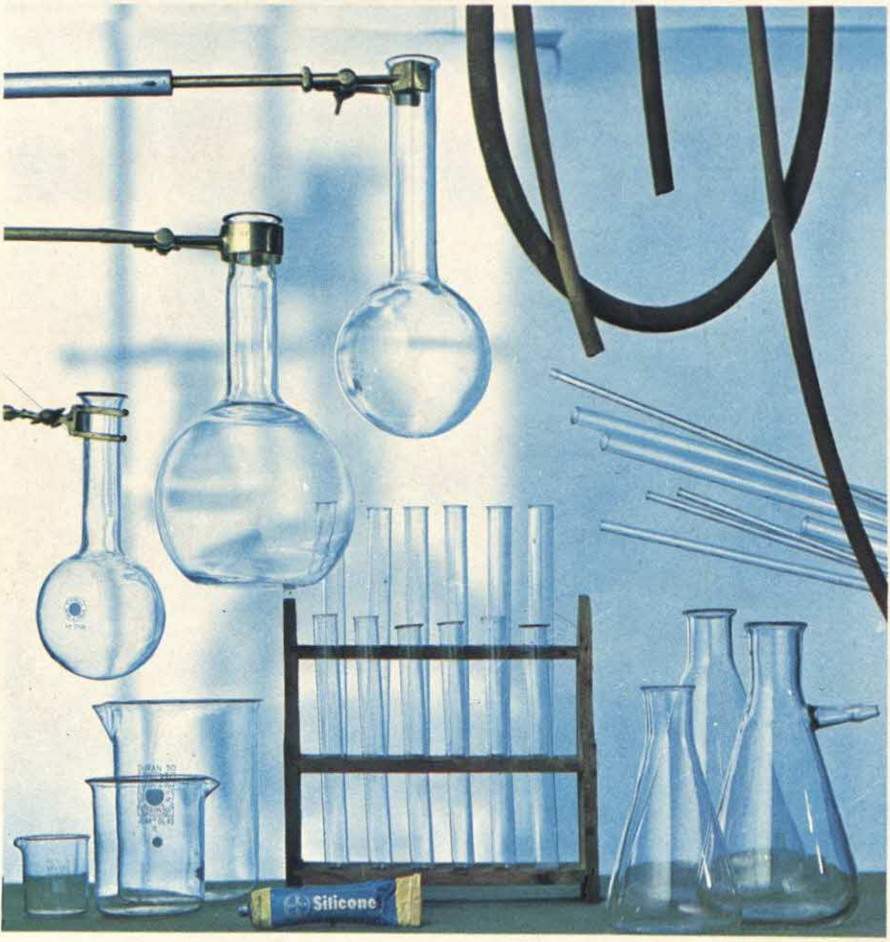

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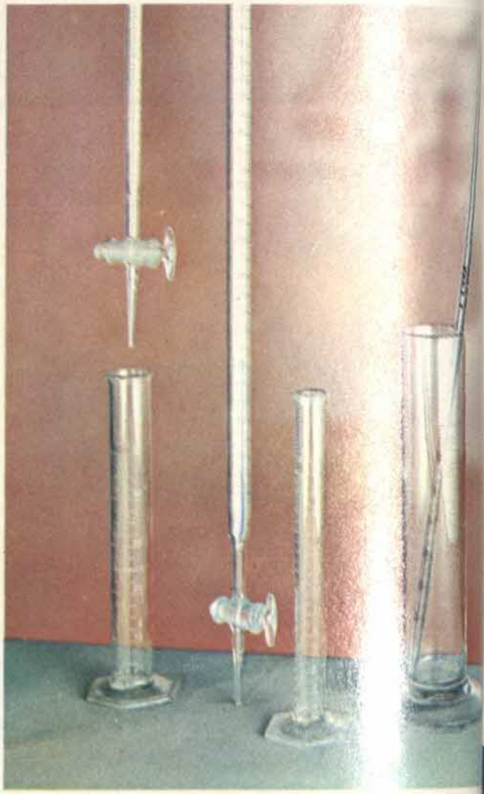

CALIBRATED GLASSWARE — Together with ordinary glassware, it is essential to have a complement of calibrated glass equipment. The cylinders on bases (Illustration 8) are called graduates, and come in sizes ranging from 10 ml to over 1 l in capacity. A pipette stands in one of the graduates, and is used to measure volumes of less than 10 ml. The burettes are used to perform delicate measurements, such as titrations.

GLASSWARE — The commonly encountered laboratory glassware is pictured in Illustration 7. Most glassware used today is of the heat-resistant type, so that high temperatures will not render it useless. The beakers at the lower left are available in various capacities, from 5 ml to 1 l. Suspended above them are two round-bottomed flasks and a Florence flask, also available in a number of capacities. The test tubes, supported in a rack, are standard items that are found in a variety of sizes. On the right, the aspirator and two Erlenmeyer flasks complete the array of standard laboratory containers. Glass tubing comes in lengths of about 1 m (3 ft), and sports diameters of many dimensions. To link equipment together, rubber tubing of a nonreactive type is often used. To facilitate the connection of tubing to glass and metal fittings, silicone lubricant can be used, but it is wise to use the lubricant only when it will not interfere with reactions.

A PAN BALANCE—A balance is indispensable for any type of analytical work. While a complete laboratory will have an analytical balance, this is a costly and delicate piece of equipment. In its place, a used pharmaceutical balance, such as the one shown here, will suffice provided an accurate set of weights is obtained. A word of caution: weights should never be handled with the fingers, since natural oils and perspiration affect their precision. Always use the tongs provided with the set of weights. For gross weighing, an ordinary spring scale can be used, but should only be used for weights of less than 1 kg (1,000 grams).

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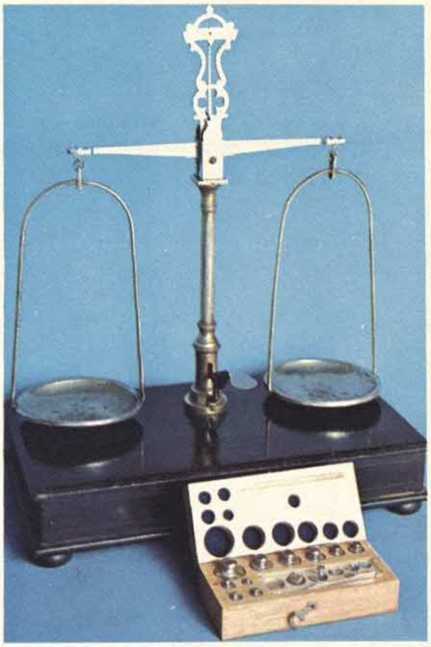

CONSTRUCTION OF A CONDENSER—As shown in this illustration, a condenser consists of two glass tubes, one inside the other. The central tube will contain the vapors to be condensed, while the outer tube functions as the cooling coil. Cold water enters the coil at the bottom, returning to a drain through the rubber tubing on top. Two-holed rubber stoppers provide the seals at both ends of the condenser.

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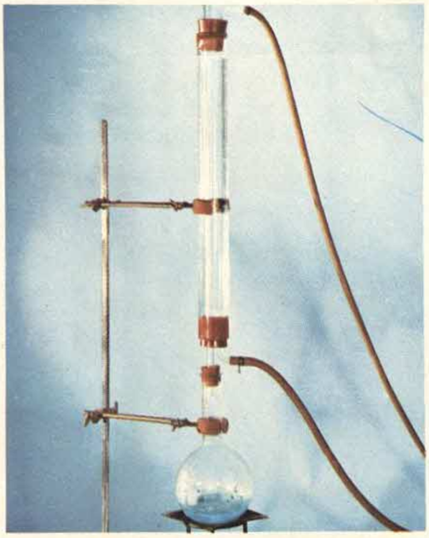
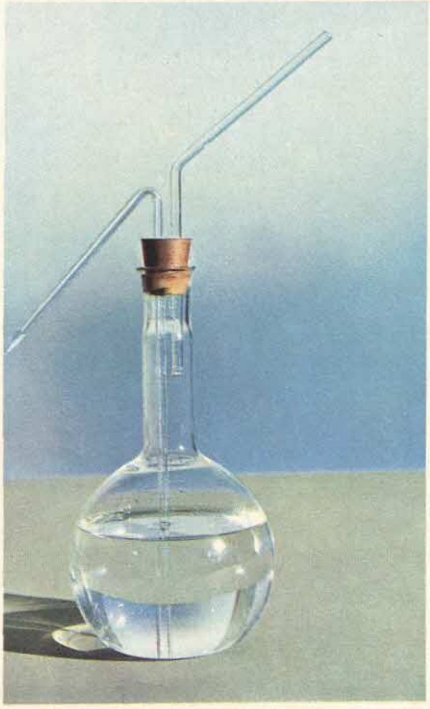


MUFFLE—A very useful accessory is the muffle, or kiln, which is really no more than an electric oven. Its advantage lies in accurate control of indirect heat for drying at low heat or turning materials to ash at high temperatures. This piece of equipment can easily be constructed at home.

11



THE WASH BOTTLE—For making precise dilutions and for washing equipment, a wash bottle is easily constructed from some glass tubing, a two-holed rubber stopper, and a Florence flask. One of the tubes serves as a fine nozzle, while the other is a mouthpiece, which should have fire-polished edges.

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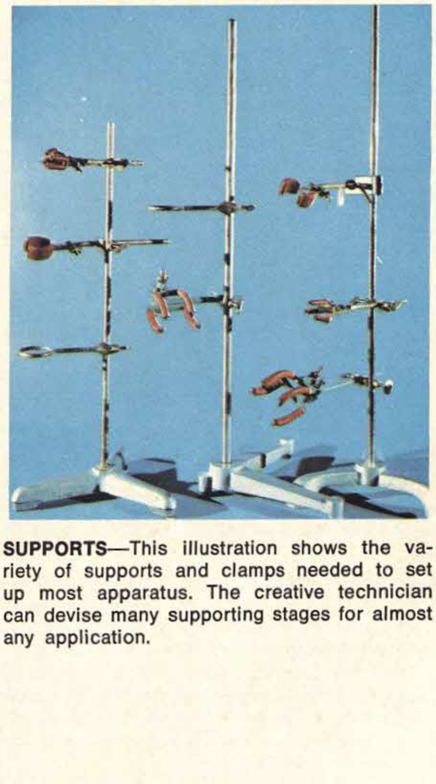


SUPPORTS—This illustration shows the variety of supports and clamps needed to set up most apparatus. The creative technician can devise many supporting stages for almost any application.

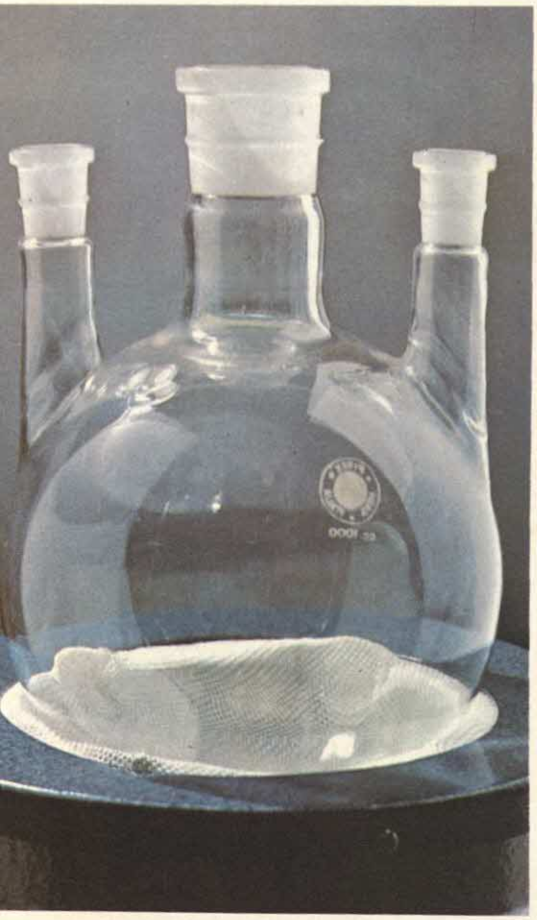
ADDITIONAL LABORATORY EQUIPMENT

filling special needs

Once the chemical laboratory has been equipped with the basic apparatus and the first few experiments have been completed successfully, the average experimenter will want to expand his horizons. While the materials previously described are quite sufficient to perform hundreds of analyses, it will soon become apparent that new and perhaps specialized equipment must be obtained. This is especially true in organic chemistry.

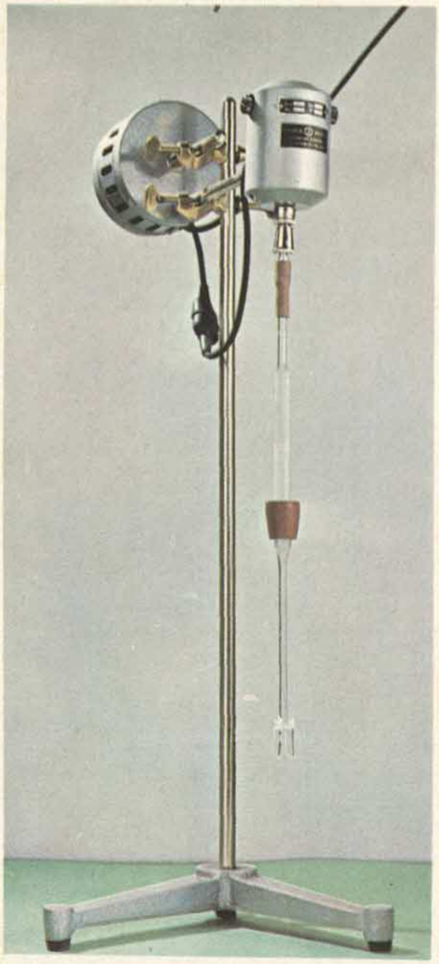
Work in organic chemistry requires careful thought as to the type of equipment selected for any given experiment. This is because the conditions inherent to an organic reaction are often many in number. Of course, not all reactions in organic chemistry are insurmountably complex, but even those that are relatively simple do indicate the use of somewhat out-of-the-ordinary apparatus.

The equipment described here represents just some of the many types available from which complex constructions can be made. The complexity of the apparatus is directly related to the complexity of the experiment.

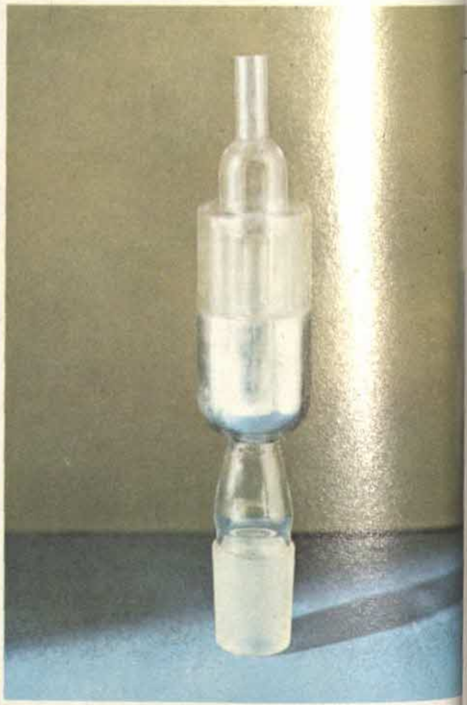


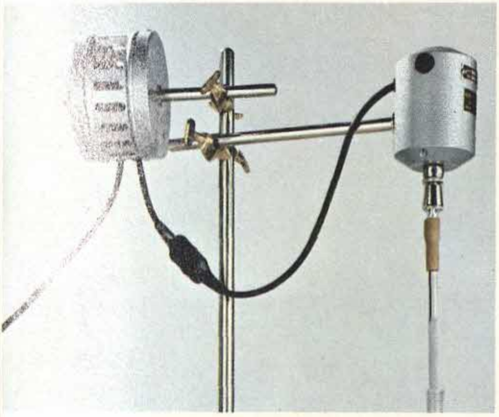
REACTION FLASK — Generally, when more than one operation is to be carried out simultaneously, a three-necked reaction flask is used. The interiors of the upper sections of the necks are precision ground and provide fittings for other pieces of equipment. The flask shown here has a capacity of 1 liter (about 1 qt), but the size chosen will depend on the volume of reactants.

MOTOR DRIVEN STIRRER—In many experiments, the contents of the flask must be kept in constant motion so that none of the reactants is excluded from the reaction. Usually made of glass, the stirrer fits into the flask through the center neck. Where a completely closed stirring operation is required, powerful magnets provide a magnetic coupling between the stirrer and the motor shaft.



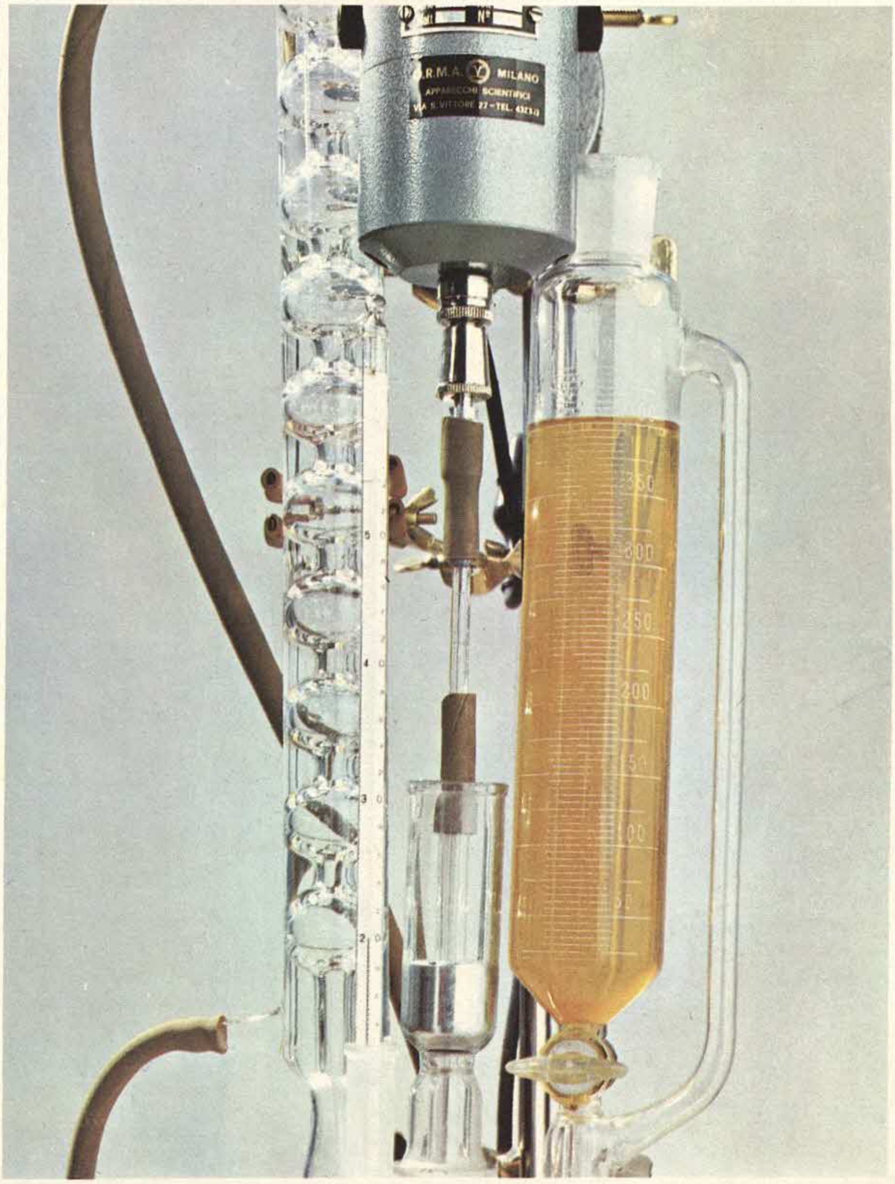
MERCURY JOINT—When mechanical stirring is used and air must be excluded, a seal must be maintained at the point where the stirring rod enters the flask. One way to do this is with a mercury joint. The shaft of the stirrer is connected to the center rod in the joint, and the mercury ensures an adequate seal. The ground portion of this equipment fits perfectly into the center neck of the flask.





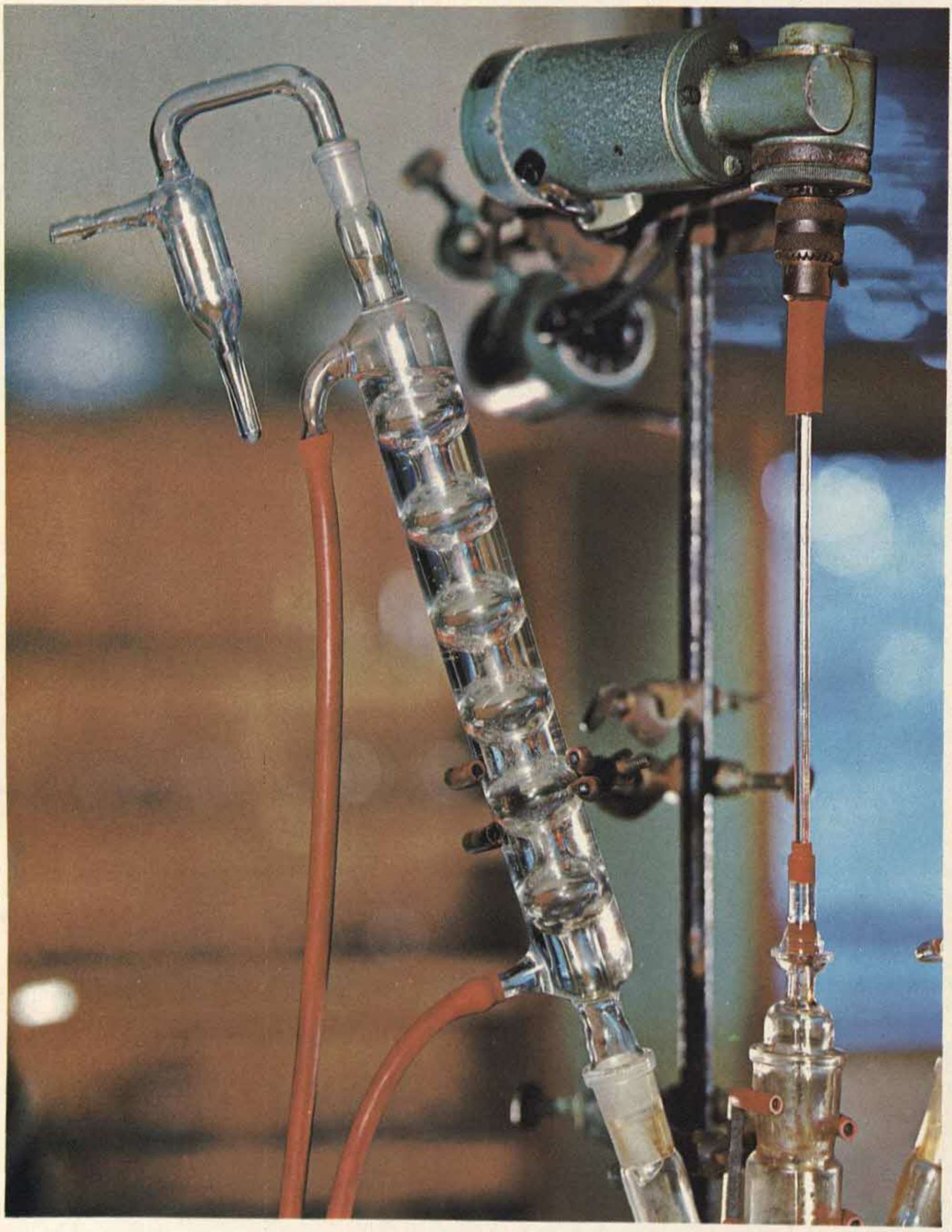
THE STIRRER MOTOR—A small electric motor provides the power for the stirrer. The motor's speed is regulated by a rheostat.

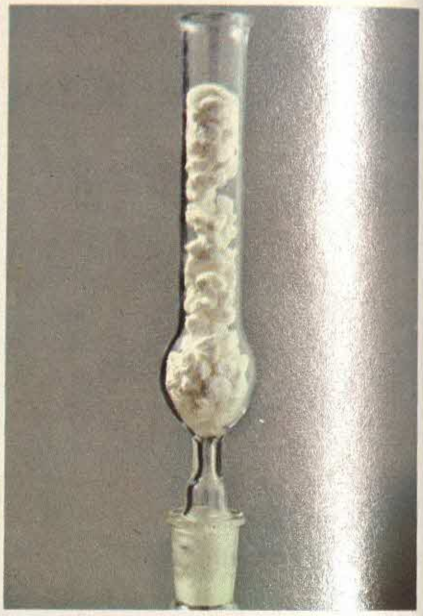
THE STIRRER AT WORK—The whirling of the stirrer keeps all reactants in constant contact. The rhythm of agitation must be monitored because if the entire shaft of the stirrer from the motor through the joint and into the flask is not exactly vertical, the motor may heat up with a subsequent change in the number of revolutions per minute.



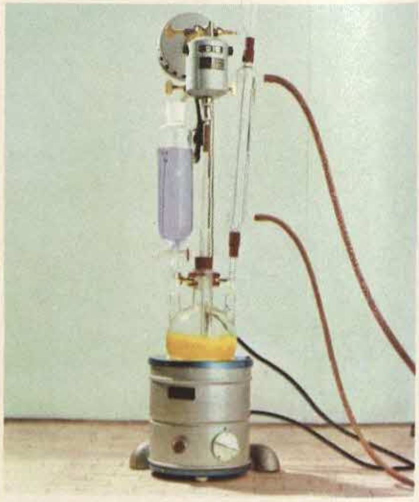
CONDENSER—To maintain the volume in the flask, a condenser is fitted to one of its necks, in this case the one on the left. The condenser causes vapors rising from the heated flask to condense and fall back into the flask. The bubble-like column is inside an outer jacket, and is cooled with water that enters from the bottom and returns to a drain from the top. If the reaction in the flask occurs between substances having boiling points above 200° C (392° F), cooling and condensation is accomplished with air. If water were used, the glass condenser would probably shatter due to extreme temperature differences.

GAS-PRODUCING REACTIONS—This illustration shows a condenser to which a special gas detection device has been fitted. In certain reactions it is important to know if gas is being liberated even though condensation is taking place. If gas is escaping, it will rise through the condenser into a capillary inside the device. Since the capillary has one end immersed in water, a series of bubbles indicates the presence of the gas.

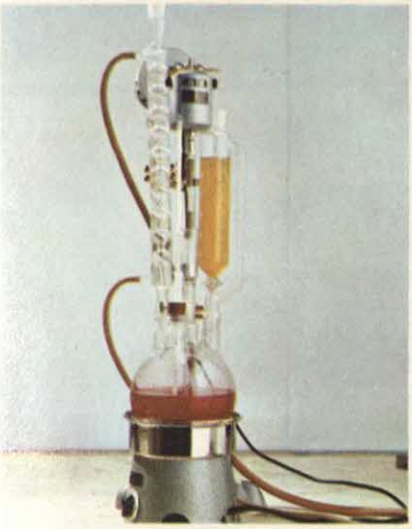




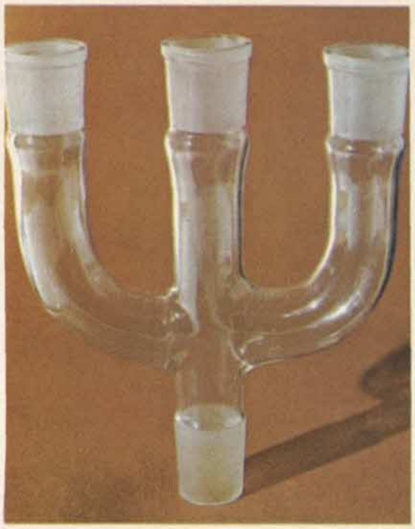
CALCIUM CHLORIDE TUBE—If atmospheric water vapor is to be excluded from the reaction flask, the condenser must be sealed. An ordinary glass stopper will not work because there will always be a leak in the seal caused by pressure within the condenser. Therefore, a tube containing a hygroscopic material (calcium chloride or silica gel, for example) is used. This apparatus traps the slightest trace of humidity in the air.



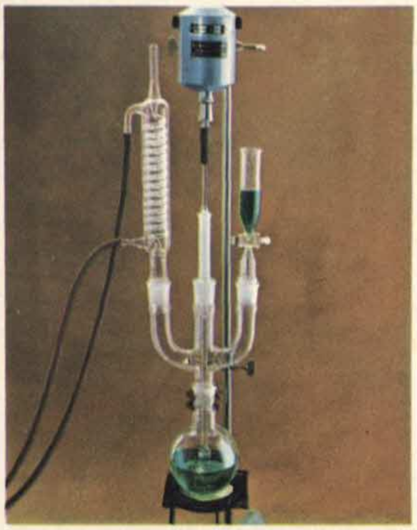
DROPPING FUNNEL—In most organic reactions, one reagent is slowly added to another already in the flask. This is done with a dropping funnel (seen on the left), the flow of which is regulated by a stopcock. The funnel, with its stopcock closed, is filled with reagent and inserted in one of the flask's necks. By opening the stopcock slowly, the liquid falls into the flask drop by drop.



DROPPING FUNNEL WITH SIPHON—This piece of equipment is especially useful when conducting reactions in the absence of oxygen from the air. Many substances are unstable in air, being either oxidized or hydrolyzed. Thus, it is necessary to provide an inert atmosphere inside the flask. To do this, a four-necked flask is used; the fourth neck is attached to a nitrogen source. This inert gas can rise through the siphon of the dropping funnel, itself sealed at the top, to replace the atmospheric oxygen. The nitrogen is supplied from standard laboratory cylinders.



CANDELABRUM—Looking like a candle, from which it takes its name, the candelabrum effectively doubles the function of each neck on the reaction flask. Thus, a three-necked flask can be fitted with a considerable number of instruments or pieces of equipment when such a device is used.



APPLICATION OF A CANDELABRUM—When the volume of reagents is small, it is often practical to use a small flask with a single neck. To fit all the necessary equipment to the flask, a candelabrum is attached to the flask as shown, creating, in effect, a miniature three-necked flask.

CHEMICAL ATTACK

When conventional laboratory equipment is subject to chemical attack, special equipment is necessary. Rubber tubing, for example, is subject to chemical attack by aromatic solvents, resulting in damage to the tubing and contamination of the reagents. In such a case, polyethylene tubing is often used; it is chemically inert and is unaffected by most acids and alkalies. Another tubing material is neoprene, a synthetic rubber highly resistant to oils, gasoline, sunlight, ozone, and heat. Neoprene tubing also has a lower permeability to gases than rubber.

Metals can be corroded chemically through oxidation, or electrochemically through the flow of electric current in an aqueous solution. In addition, corrosion rates increase with increasing temperature, which results in greater ionization of solutions. Chrome or zinc plating, glass coating, or plastic coating of laboratory equipment often provides effective protection against most types of corrosion. A knowledge of resistance of materials to chemical attack and corrosion is of great practical value to the chemist.

HIGH TEMPERATURES

When an experiment or analysis requires extremely high temperatures or sudden extremes of temperature, special types of containers may be required. Vycor—a type of glassware having a low coefficient of thermal expansion and a high melting point—is frequently used in place of conventional glassware. When high corrosion resistance at extreme temperatures is required, Teflon vessels are sometimes used. Crucibles made of fused silica are used when substances must be heated up to 1,450° C (2,642° F).

ELECTRIC HEATER—Because many organic reactions cannot be carried out in the presence of an open flame (for reasons of safety), an electric heater is an essential piece of equipment. The heat produced can be accurately controlled to maintain a constant temperature for as long as necessary.

LABORATORY GLASS—I

basic glassworking

Although most of the glassware encountered in a modern chemistry or physics laboratory can be obtained commercially, it is sometimes necessary to construct apparatus for a specific purpose. In such instances, a basic knowledge of glassworking is required.

Working with glass is neither difficult nor dangerous, and can be highly interesting, provided a few simple precautions are observed. However, in order to work glass successfully some of its characteristics must be understood.

WHAT IS GLASS?

Strange as it may seem, glass is classified physically as a liquid, although its extremely high viscosity gives the material all the qualities normally associated with solids. Glass has no definite melting point, but becomes soft over a range of increasing temperatures, ultimately reaching the point where it becomes liquid in the true sense. Furthermore, during the softening process the solid phase and the liquid state never occur together.

Another fact attesting to the liquidity of glass is its ability to be shaped when cold without machining. This, however, requires an extremely long time, perhaps hundreds of years.

Chemically, glass is a mixture of many compounds, the most prominent being common sand, or silicon dioxide. Ordinary glass also contains compounds of boron, sodium, iron, and other elements. These compounds cannot be called impurities in the strictest sense because they lower the melting point of silicon dioxide, which melts above 1,600° C (2,912° F).

Because glass must suit a variety of needs, no one type is practical for all applications. Hence, depending on its use, the chemical and physical properties of glass can be tailored for a specific objective. Certain types of glass, for example, do not soften under heating conditions normally encountered, and so are used for cooking equipment and laboratory apparatus. Others soften at little more than 500° C (932° F)—common glass is an example—and can be easily worked. Glass can be manufactured to resist extremes of heat and cold, to withstand mechanical shock, or to shatter at the slightest stress.

Each of these properties has its effect on glassworking techniques. In the home, it is difficult to work with glass containing a large percentage of silicon because of the high temperature required for softening. Common glass can easily be worked in the flame of a kitchen stove.

RAW MATERIAL

The simplest operations can be carried out by the use of glass tubing, and for everyday laboratory use so-called "soft glass" is commonly employed.

In order to work glass tubing successfully, the flame from the heat source must be large enough to surround the tube. If the size of the tube stock is increased, the flame must be made proportionately larger and hotter. In the laboratory, an ordinary Bunsen burner is sufficient for most operations. Glass with a high softening point requires special equipment to add oxygen to the gas mixture.

CUTTING THE TUBE STOCK

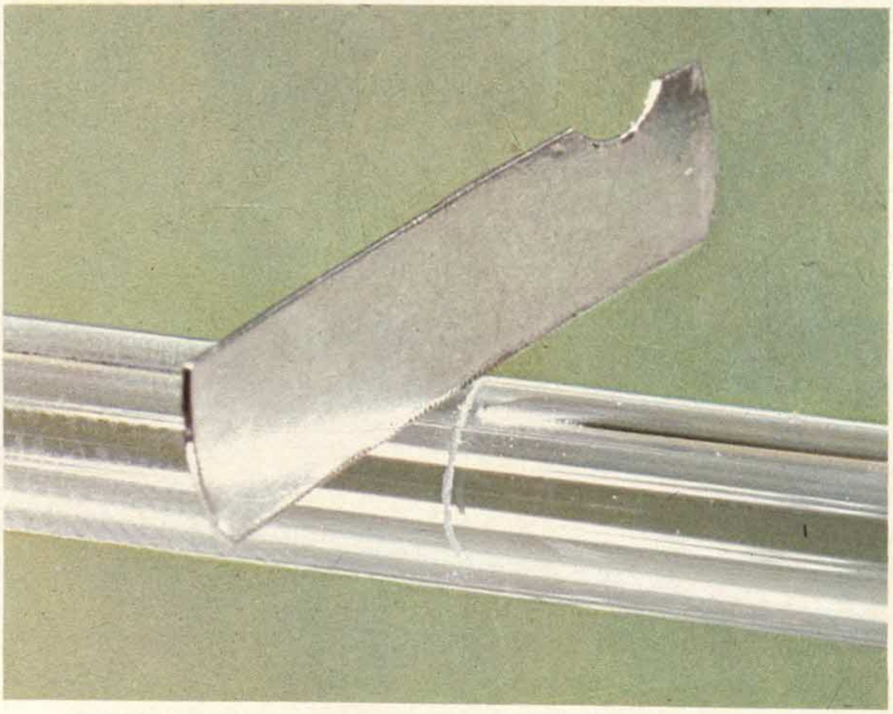
Glass tubing is sold commercially and is usually available in lengths of one yard or one meter. Thus, the first step in the construction of a piece of equipment is to cut the stock to the correct length. This is quickly done by filing a small nick at the point where the tube stock is to be cut. Then, with the tube grasped firmly in both hands, thumbs opposite the nick, a steady, quick pressure exerted by the thumbs will cause the tube to snap neatly. (For safety's sake, it is best to wear leather gloves or wrap the tubing in several layers of cloth.)

THE GAS FLAME

For most glassworking, the Bunsen burner found in all laboratories is ideal. This

1

CUTTING GLASS TUBING—The file shown in this illustration is specially made for cutting glass. An ordinary tool shop file will suffice, however. Once a nick has been made in the tube, the glass will break evenly under pressure exerted by the thumbs set opposite the groove. It is advisable to wear leather gloves to protect the hands.



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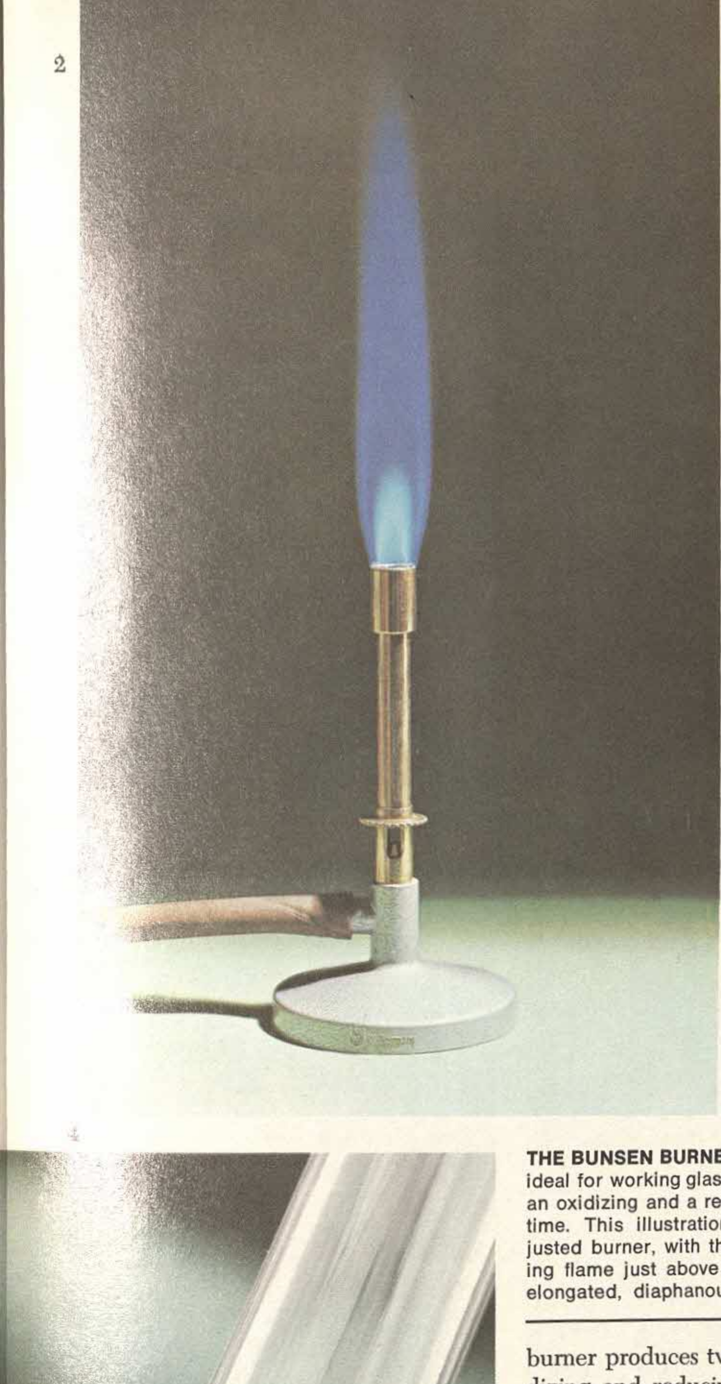

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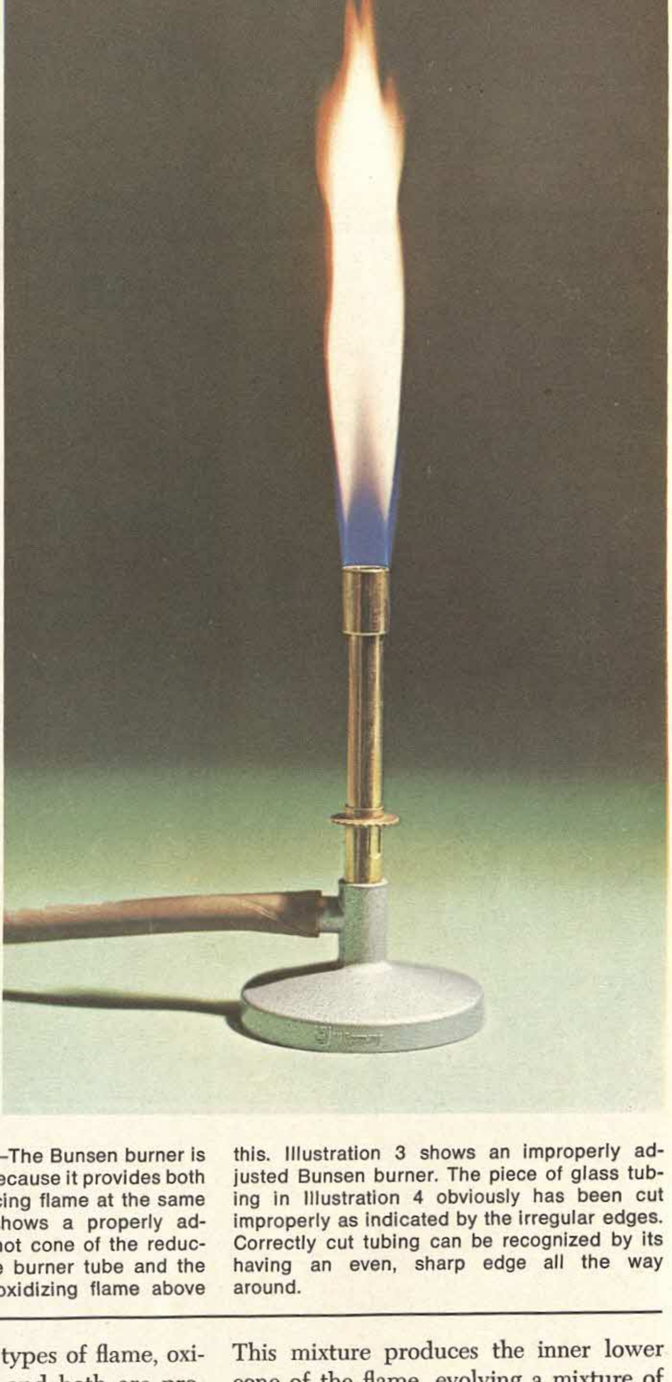

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THE BUNSEN BURNER—The Bunsen burner is ideal for working glass because it provides both an oxidizing and a reducing flame at the same time. This illustration shows a properly adjusted burner, with the hot cone of the reducing flame just above the burner tube and the elongated, diaphanous oxidizing flame above this. Illustration 3 shows an improperly adjusted Bunsen burner. The piece of glass tubing in Illustration 4 obviously has been cut improperly as indicated by the irregular edges. Correctly cut tubing can be recognized by its having an even, sharp edge all the way around.

burner produces two types of flame, oxidizing and reducing, and both are produced at the same time. Nearest the burner tube is a small, very hot cone of fire. In a properly adjusted burner, this reducing flame is a bright blue. Above this is an elongated, diaphanous tail of flame, lighter in color, and relatively cool compared to the reducing flame. This is the oxidizing flame. The amount of oxygen from the air that is mixed with the gas determines whether a flame will oxidize or reduce a material.

The Bunsen flame results when air and gas are admitted in the proportion of about three volumes of air to one of gas. This mixture produces the inner lower cone of the flame, evolving a mixture of water vapor, carbon monoxide, hydrogen, carbon dioxide, and nitrogen. The water vapor and nitrogen reach the outer combustion zone where the water gas becomes burned up by the ordinary, or secondary, air supply. Metallic salts impart characteristic coloration to the flame.

For many glassworking operations, the burners of a gas kitchen stove will suffice. Such burners are adjusted so that the flames are always reducing. A disadvantage is that the flames are arranged in a small circle and do not produce a single, strong flame.

FIRE-POLISHING THE TUBE ENDS

When a glass tube has been cut properly, the cut end will appear to be even and smooth all the way around. However, it is really quite sharp. Rounding the cut ends by an operation called fire polishing is quite simple. First, the end of the tube is heated in the oxidizing part of the flame while being rotated to heat all sides equally. After about 15 seconds of preliminary heating, the tube end is heated strongly, while still being rotated, at a point just above the tip of the reducing flame. In a very short time the flame takes on a bright yellow-orange color and the glass becomes red-hot and pliable. The coloring of the flame is due to the vaporization of sodium atoms in the glass. At this point, the rounding of the cut end is complete, and the tube is removed from the flame and set aside to cool.

Even though the glass may not appear hot, it is! Heating does not discolor glass, and because glass is a very poor conductor of heat it will remain very hot for some time. Care must also be taken to keep water away from all glass being worked. Any water on the stock material will cause the glass to shatter violently in the heat of the flame. If heated glass is placed in water it, too, will shatter.

Cooling is best accomplished by setting the tube on a piece of dry asbestos. Once the tube has cooled completely, the other end should be rounded in the same way.

MAKING A TEST TUBE

Although it is seldom required because test tubes are easily purchased, the tech-

FIRE POLISHING—The sharp edge of a newly cut glass tube is rounded, or fire-polished, using a Bunsen burner. The hottest point of the flame is just above the reducing cone. When the glass reaches red heat, it softens to form a rounded edge, and turns the gas flame orange-yellow (Illustration 5) because of vaporized sodium in the glass. Illustration 6 shows a properly fire-polished glass tube.

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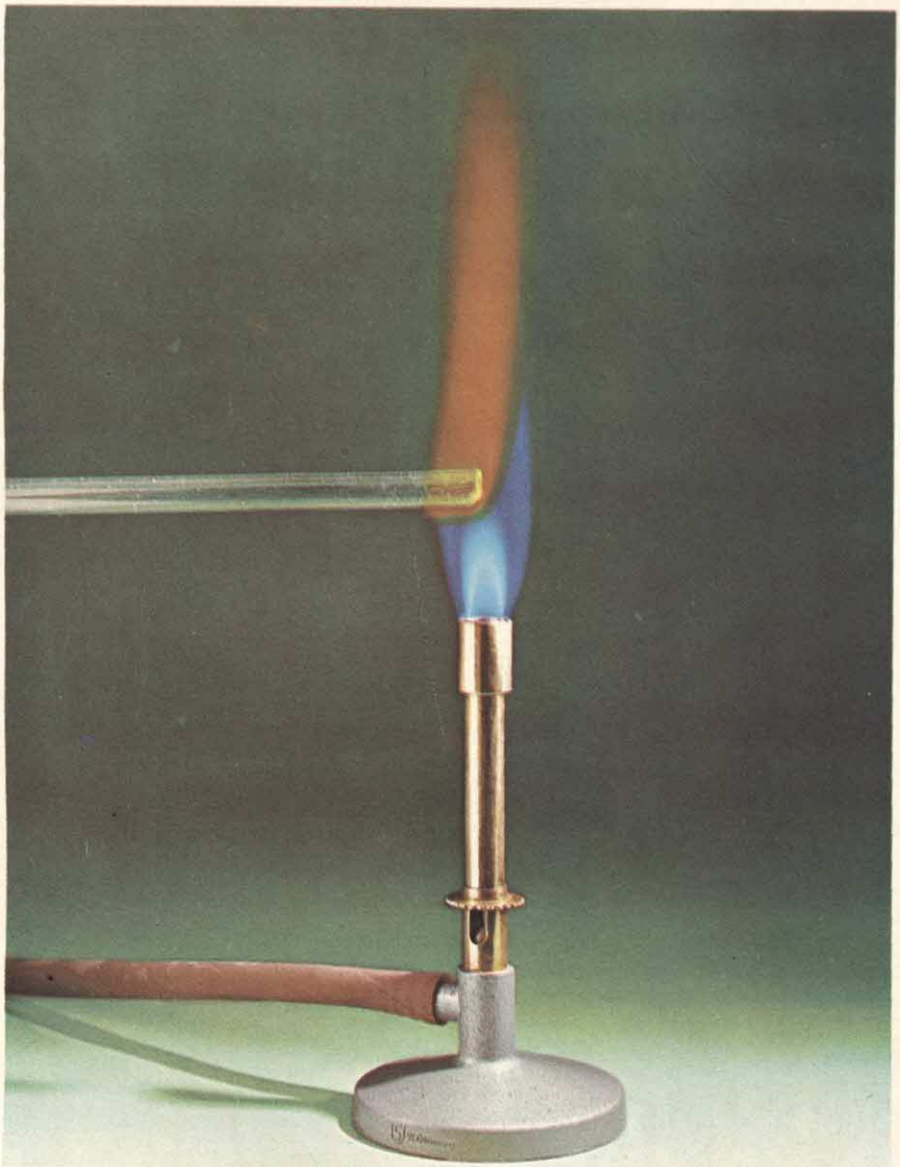

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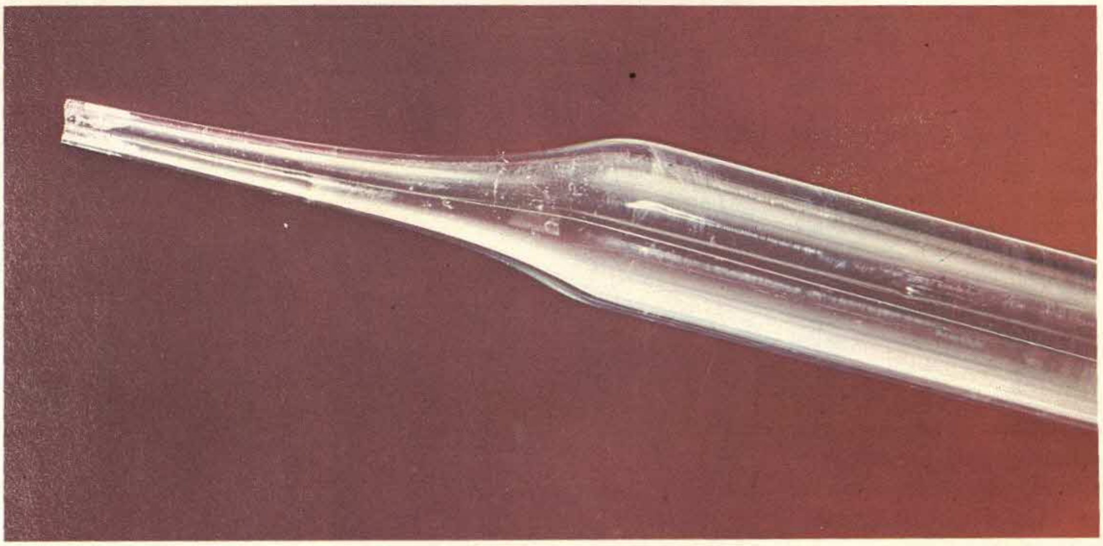

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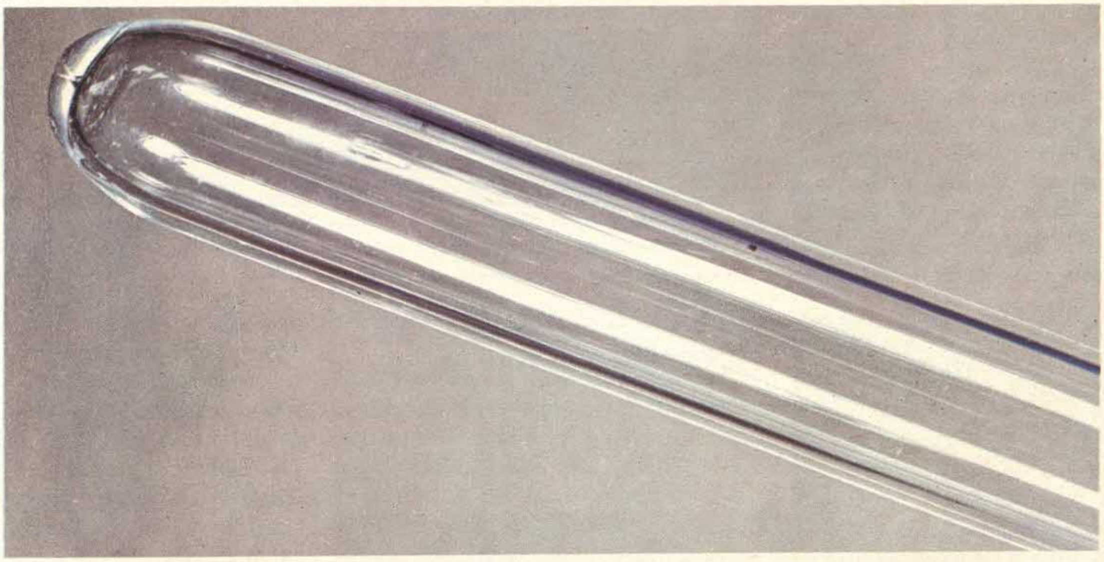

CLOSING A GLASS TUBE—This capillary (Illustration 7) has been pulled in preparation for closing a glass tube. When placed in the burner flame, the capillary will soften and close almost immediately because of its small diameter. The softened glass forms a small sphere. The nicely rounded end of the closed tube shown in Illustration 8 has been shaped with a graphite spatula.

nique for closing a glass tube is worth knowing. In fact, there are applications for closed tubes other than test tubes, and the following procedure can be used in such instances.

The first step in closing a tube is to select a piece of glass stock several inches longer than the tube length desired for the finished product. This provides a handhold at both ends of the stock, eliminating the possibility of being burned by hot glass.

The point of closure is heated uniformly by rotating the stock first in the oxidizing flame, and then in the reducing flame. When the flame becomes yellow, and there is a noticeable flex to the red-hot glass, the tube is removed from the flame and pulled sharply. The glass becomes elongated, narrowing at the point where the tube is hottest, forming a capillary. This thin section cools almost immediately, and the tube can easily be snapped in two. (Although the capillary cools, the rest of the tube remains very hot, and care in handling is advised.)

The end of the tube to be closed is again placed in the flame and the capillary melts immediately, closing the tube. To give a rounded shape to the closed end, the tube is heated a final time, and is formed with a graphite spatula. Should the closed end appear too flat, the tube is reheated. A short burst of breath blown into the tube will cause the flat end to bulge. A little practice will indicate how much air must be blown into the tube to obtain the proper roundness. The tube is now cooled on a dry surface.

LABORATORY GLASS—II | advanced techniques

The successful working of glass is a skill gained by experience. A little practice will remedy most faults, and can result in the construction of interesting and unique pieces of equipment.

Whenever glass is worked, the standard precautions must be taken to prevent injury. For example, heated glass does not become discolored, and once the red glow of softened glass has subsided there is no way, visually, of determining whether glass is hot. (Many fingers have been burned through careless handling.) It is mandatory that all glass to be worked in a flame be absolutely dry, since water will cause hot glass to shatter. Finally, when cutting or breaking glass stock, it is advisable to protect the hands, either by wearing leather gloves or by wrapping the stock in several thicknesses of cloth.

MAKING CAPILLARIES

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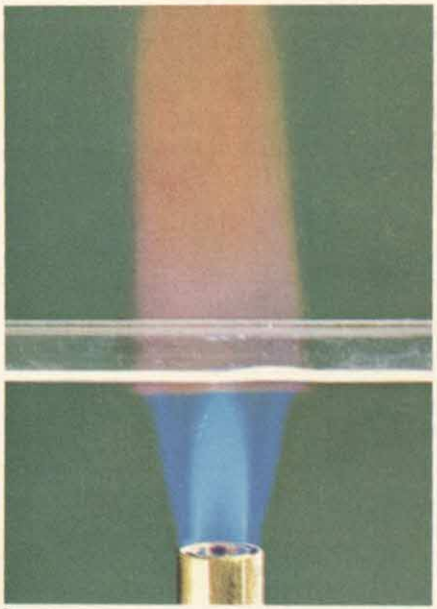

PLACEMENT OF THE TUBING IN THE FLAME—The first step in making a capillary is placing the tube stock in the hottest part of the flame, and constantly rotating the tube to ensure uniform heating.

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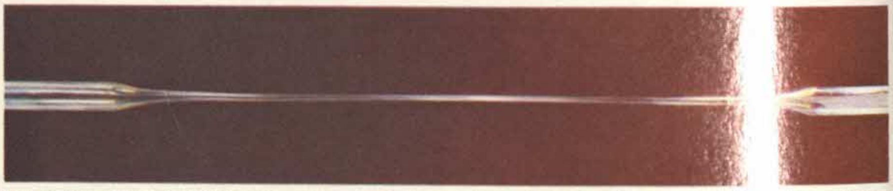

DRAWING THE CAPILLARY— Once at the proper temperature, the tube stock is withdrawn from the flame and pulled. The softened part elongates, forming the capillary tube.

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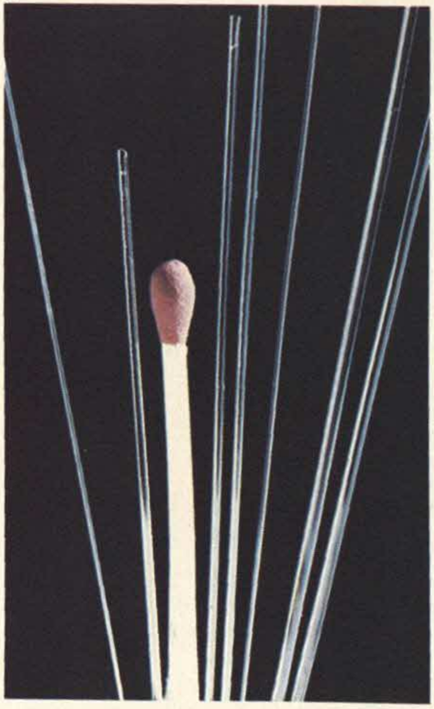

CAPILLARIES—Capillaries are extremely thin glass tubes, whose sizes are compared to an ordinary match in the illustration.

Many experiments require tubes having very small interior diameters, often less than one millimeter. With a properly adjusted Bunsen burner and glass tube stock of moderate dimensions, it is an easy matter to make capillary tubes for almost any purpose.

The basic material is glass tubing stock at least 10 cm (about 4 in.) long, with an external diameter of 5 to 10 mm (about 0.2 to 0.4 in.) and a wall thickness not less than 1 mm (about 0.04 in.). To form a capillary, the stock is held at both ends and the center part is rotated above the reducing flame until it softens (see Illustration 1). It is essential that all sides of of the tube are heated evenly. When the tube becomes flexible, it is withdrawn from the flame and pulled immediately, elongating the softened part and greatly decreasing the tube's diameter. As Illustration 2 shows, the original tube is tapered in the center into what appears to be a thread. In fact, this is a capillary; the rapid elongation does not close the tube, but simply makes it thinner.

A capillary as long as that illustrated (about 0.5 m in length) is required only rarely, and it should be cut into shorter pieces about 10 to 15 cm (about 4 to 6 in.), for two reasons: ease of application, and because the section is not uniform throughout its length, being slightly larger at the ends and smaller at the center.

The general uniformity of the capillary tube can be determined visually without aid. However, to measure its diameter requires the use of a microscope. The simplest way to do this is to break off a small piece of the tube and insert it vertically into a bit of modeling clay on a microscope slide. Such measurements must be made when capillaries are used for such precise analytical laboratory work as capillarity of fluids and expansion of gases.

A similar technique is used in making a jet point. A jet point is a point like that on the end of the glass tube in a medicine dropper. The softened and stretched tube is allowed to cool, then cut off at the point where it tapers to the desired diameter. The cut end may be rotated in the flame to smooth the edges, and a rubber bulb attached to the other end if it is to be used as a dropper.

BENDING GLASS TUBING

While it is not difficult to bend glass tubing per se, some skill is required to do so in such a way that the bend does not narrow. The secret, if it can be called that, lies in the proper heating of the tube stock.

A length of stock that will allow it to be held at both ends during the heating and bending operation is the first requirement. At the point where the bend is to occur, the tubing is heated slowly with constant rotation so that all sides of the tube are heated equally. When the tube just begins to flex, and only a hint of red

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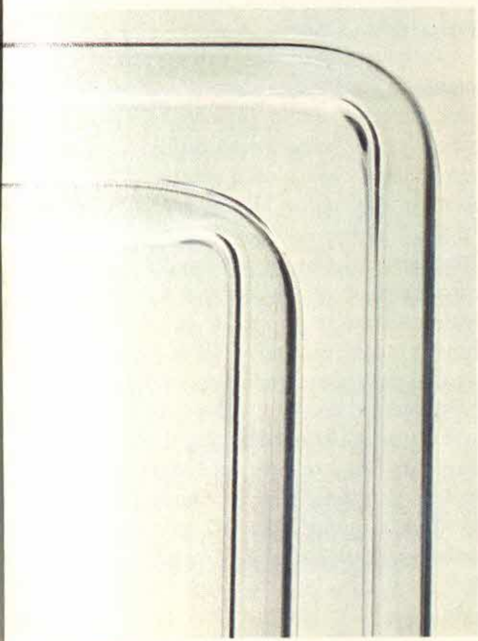

90° BENDS—Right angle bends demonstrate the results of good technique and poor procedure. The upper tube is a perfect bend, with a constant inside diameter. The lower example shows what happens when the tubing is not heated uniformly.

glow has appeared, the tube is removed from the flame. With slight pressure the tube is immediately bent *in one direction only*; the bending is stopped when the desired angle is reached. The total operation should take only a minute or so for normal-sized tubing. If the interior dimension of the bend appears unequal to the straight sections, it is best to discard the attempt and begin again. A poor bend can be remedied, but because a good bend is relatively simple to make with practice, it is a waste of time to try and rectify any mistakes.

SEALING GLASS TUBING

Although making a successful glass seal requires a good degree of skill, serviceable ones can be formed with a bit of practice. Unlike other types of constructions, seals cannot be made without an intense heat source such as a laboratory burner. Kitchen stoves do not provide the pinpoint heat required.

In any operation involving the joining of one piece of glass to another it is essential that both pieces of glass be of the same type. Different kinds of glass expand and contract at different rates; it might be possible to join two tubes of different composition so that the seal appeared perfect while the glass was soft but as it cooled the seal would be likely to break apart.

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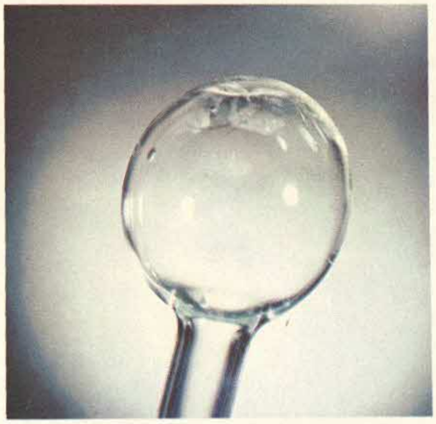

GLASS BUBBLE—Before making a glass seal with tubing, one end of the tube is closed. Air blown into the open end causes the formation of a bubble, if the glass is hot enough.

The kind of glass used in most laboratory ware is a soft or lime glass that melts at a relatively low temperature and is easily worked. For special purposes, a harder, heat-resistant glass containing borosilicates is used; it is similar to the glass used in heat-proof cooking utensils. Obviously, glass tubing of the two different kinds cannot be joined by heat-sealing.

A good place to start is with the sealing of two lengths of tubing in a straight line. First, one end of each tube is closed, as in the making of a test tube. It is not necessary to have perfectly rounded ends.

Next, the closed ends are each reheated until they become very soft and pliable, at which point air is blown into the tube. This results in the formation of a bubble, as in Illustration 5. Continued air pressure will cause the bubble to burst (see Illustration 6), forming a rough flange (Illustration 7).

Now, the flanged ends are heated together just above the reducing flame while the tubes are constantly rotated to ensure even heating. When it is seen that the glass is softened, very slight pressure exerted from the ends of the tubes will cause the two sections to fuse. The seal is perfected by: (1) continued heating and rotation; (2) allowing the joint to shrink; (3) puffing gently into the tube to expand the joint slightly; (4) stretching the joint until it is back to its original diameter. A minute or so of cooling in the oxidizing flame followed by complete cooling to room temperature results in a seal like that in Illustration 8.

Generally, there is no need to make straight-line seals as described above, since tubing can be purchased in lengths for most any purpose. However, the pro-

THE BUBBLE BURSTS — Continued heating and air pressure within the tube bursts the bubble, forming a rough flange. The ends can be heated and resealed, however.

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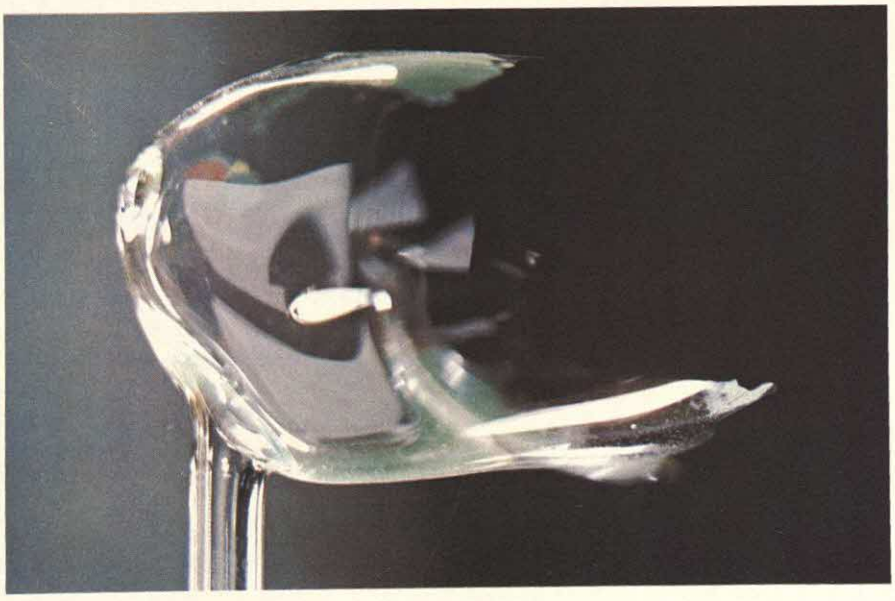

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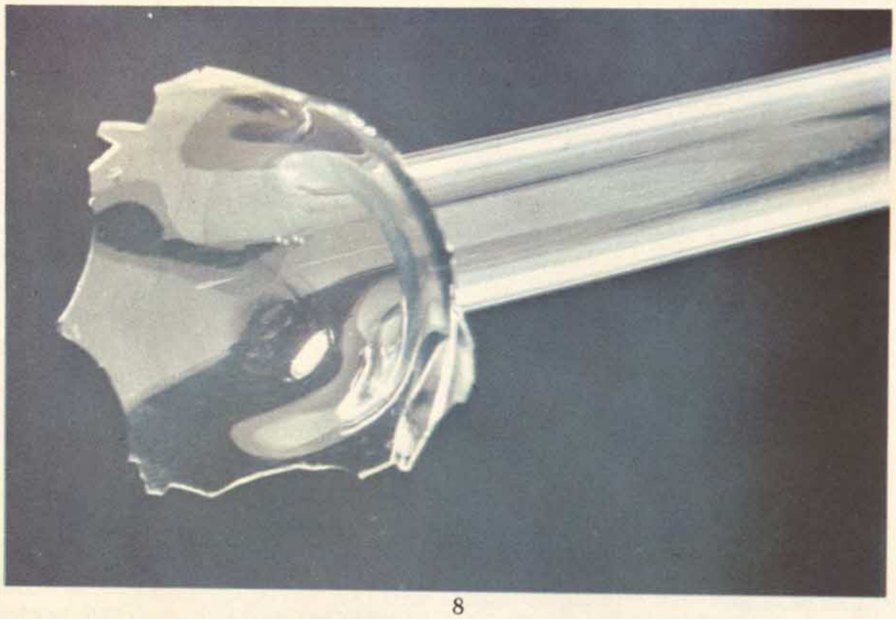

CREATING A FLANGE FROM THE BURST BUBBLE—Only a section of the bubble remains to form the flange. When two such flanges are heated together, they fuse rapidly and form a seal.

cedures are important for making other types of joints.

THE "T" JOINT

A "T" joint is just what its name implies, and is shown in Illustration 9. The technique for making one is analogous to that for making a straight-line seal. In fact, the vertical part of the "T" is prepared in the same way.

The horizontal section of the joint is sealed at its center. The flange is obtained by heating only one side of the tubing with the side or tip of the reducing flame. In this instance, the tube must not be rotated.

When the proper temperature has been reached, one end of the section is closed with the finger while air is blown into the other. The bubble that forms in the center of the tube will burst, forming the necessary flange. To seal the two sections, the procedure is identical to that already described.

ADVANCED WORK

Once these glassworking techniques have been mastered, any number of constructions can be made. Experience and the need for making unique equipment are the only guides to performing more complex operations.

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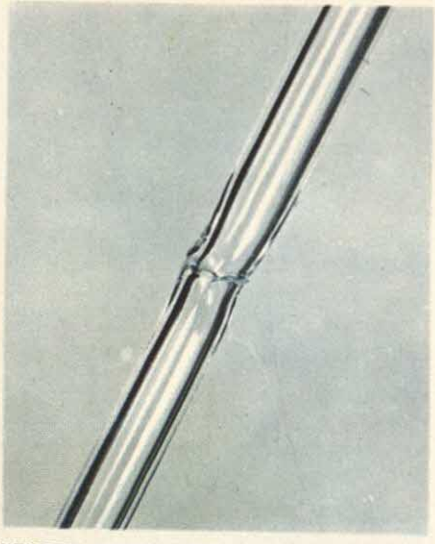

WELDED TUBES — The straight-line joint is finished by heating to smooth both the inside and outside of the tube at the seal.

Many pieces of equipment available commercially may, for one reason or another, have to be modified. This can be accomplished using these techniques. Or, specialized apparatus for a single experiment may be required—apparatus that is unavailable commercially—in which case a thorough knowledge of glass and the working of glass is called upon.

Inexpensive glass tubing may be obtained from any laboratory equipment company or firm that supplies scientific materials to schools.

Ordinary apparatus tubing, the most common kind, has a stated outside diameter. It is available in a wide range of sizes, from 3 mm (about 0.112 in.) to 50 mm (about 2 in.) in diameter. The size most useful in the laboratory is 6 mm—it fits into the holes in standard rubber stoppers and can be used with the common kind of rubber tubing that has an inside diameter of 0.224 in. The 6-mm tubing is easy to work with—not so fragile as the more slender tubing and easier to heat evenly than the wider tubing.

The special kind of tubing that is called capillary or barometer tubing has a stated inside diameter. It is commonly available in sizes ranging from 0.5 mm (with an outside diameter of 5.5 mm) to 4 mm (with an outside diameter of 8.5 mm).

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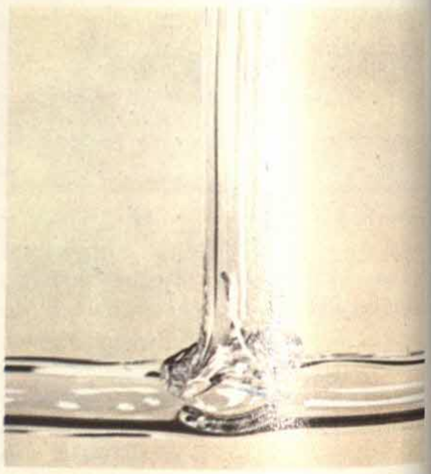

"T" JOINT — Using techniques identical to those for making a straight-line seal, other glass tubing constructions such as the "T" joints are possible. The technique is more useful for types other than straight-line seals because tubing is easy to purchase.

Glass in the form of tubing, rods, and containers is used extensively in the laboratory because it is nonporous, it can be sterilized, and it does not retain odors. Glass apparatus can be used in experiments involving most corrosive chemicals, including acids.

One exception is hydrofluoric acid, which rapidly attacks all the ordinary kinds of glass. Hydrofluoric acid can be used with only one kind of glass, a special phosphate glass patented in England in 1947.

POROSITY AND MICROPOROSITY

the permeability of matter

Porosity is a property of solid matter that permits fluids (gases and liquids) to pass through the solid by means of interconnecting cavities (pores). This property, which can be demonstrated, is a function of the structure of the solid.

Porous solids contain minute cavities or channels that interconnect throughout the solid and with its surface. These pores permit the body to absorb a certain amount of gas or liquid; the pores also permit gases and liquids to pass through the solid. A building brick, for example, appears to be a solid and compact body; yet brick is traversed by an enormous number of small canals of varying volumes that interconnect with each other. When a brick is immersed in water, it absorbs the water throughout its interior pores. The water enters the interior cavities and fills them, a fact that is easily verified by weighing the brick in its dry state and then after prolonged immersion. The increase in weight is due to the water taken up by the interior cavities, which in a typical brick occupy a volume of a few tenths of a milliliter or less.

Some solids have pores of much smaller dimensions than the pores of brick. The pores of a sheet of paper or cardboard, for example, are much smaller than those of a brick. Finally, some solids have pores of truly microscopic dimensions. A sheet of plastic, for example, is almost perfectly impermeable to liquids, yet small amounts of gases can filter through the plastic material. Using very delicate instruments, it is even possible to demonstrate porosity in a substance such as

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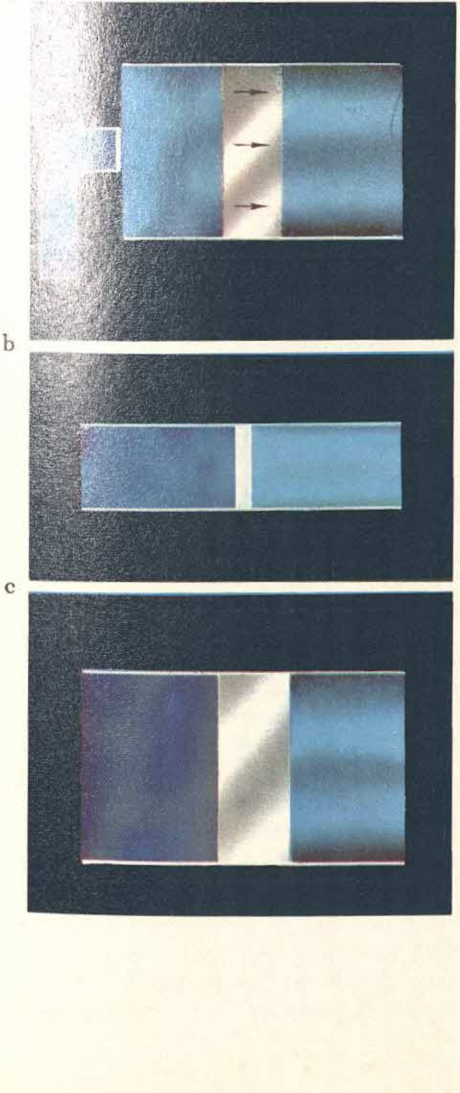

WHAT POROSITY IS—A porous body contains interconnecting internal cavities. It is not always possible, however, to study the form, dimensions, and arrangements of these cavities. In any event, this information is not always of interest. Instead, the applications of porosity are often very important. For example, it may be desirable to use a porous material for storing a gas. In such an event, it is more important to know the absorptive capacity of the solid than to understand its detailed structure.

Porosity can be defined in rather simple and yet rigorous general terms without referring to specific substances.

Porosity is defined as the ratio of the pore volume of a substance to its total or bulk volume. A measure of porosity may be obtained by determining the quantity of gas at a given pressure that will pass in unit time through a given area of a porous material of a given thickness.

Consider a tube containing a diaphragm made of a certain material (Illustration 1a). The tube to the right of the diaphragm is open to the atmosphere. A gas pump placed to the left of the diaphragm maintains a pressure against it. This pressure causes the molecules of the confined gas to pass through the diaphragm in the direction indicated by the arrows. Thus, there is a continuous flow of gas from the left to the right. Now suppose that the diaphragm dividing the tube (Illustration 1b) has a cross-sectional area of 1 cm^2; that its thickness is negligible; and that the pressure difference across the diaphragm is 1 kg/cm^2. The volume of gas in cubic centimeters passing through the diaphragm in unit time is related to the porosity of the diaphragm. Under actual experimental conditions (Illustration 1c), the pressure difference amounts to P kg/cm^2, the surface area of the sample is s cm^2, its thickness is d cm, and the quantity of gas that has passed through it in t seconds is V cm^3. The expression for porosity is, therefore,

$$V \times \frac{d}{s} \times t \times p.$$

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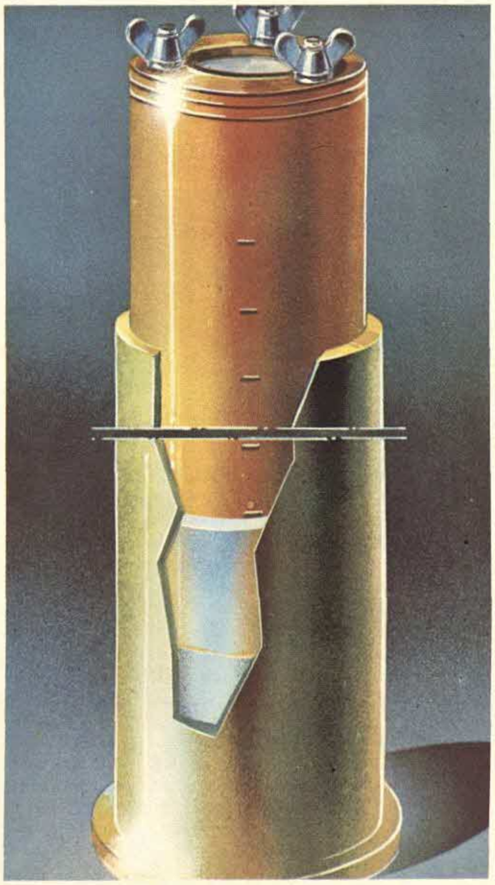

THE PRINCIPLE OF THE POROSIMETER—Several different types of porosimeter are used. The model shown here is an extremely simple one. The apparatus consists of a cylindrical container made of metal and filled with light oil or kerosene. This outer cylinder houses a second cylinder that is open at the bottom and closed at the top by means of a removable ring. This ring holds the sample of porous material by means of a rubber gasket. The weight of the inner cylinder compresses the air trapped between the sample and the surface of the liquid. This air slowly passes through the sample, and the inner cylinder sinks deeper into the liquid. A scale marked on the outer surface of the inner cylinder indicates the volume of air that passes through the sample. This volume is easily calculated when the internal diameter of the cylinder is known. A measurement with this instrument is carried out by fastening the sample in place at the top of the inner cylinder, which is then introduced into the larger one. The inner cylinder sinks down as air passes through the sample; at a certain point the first mark on the scale coincides with the upper edge of the outer cylinder. A stopwatch is started at this point; it is stopped when the second mark reaches the upper edge of the outer cylinder.

Knowing the difference in pressure between the inside and the outside of the inner cylinder, the area of the sample, and the time required for the gas to flow through the sample, the porosity of the sample can be calculated.

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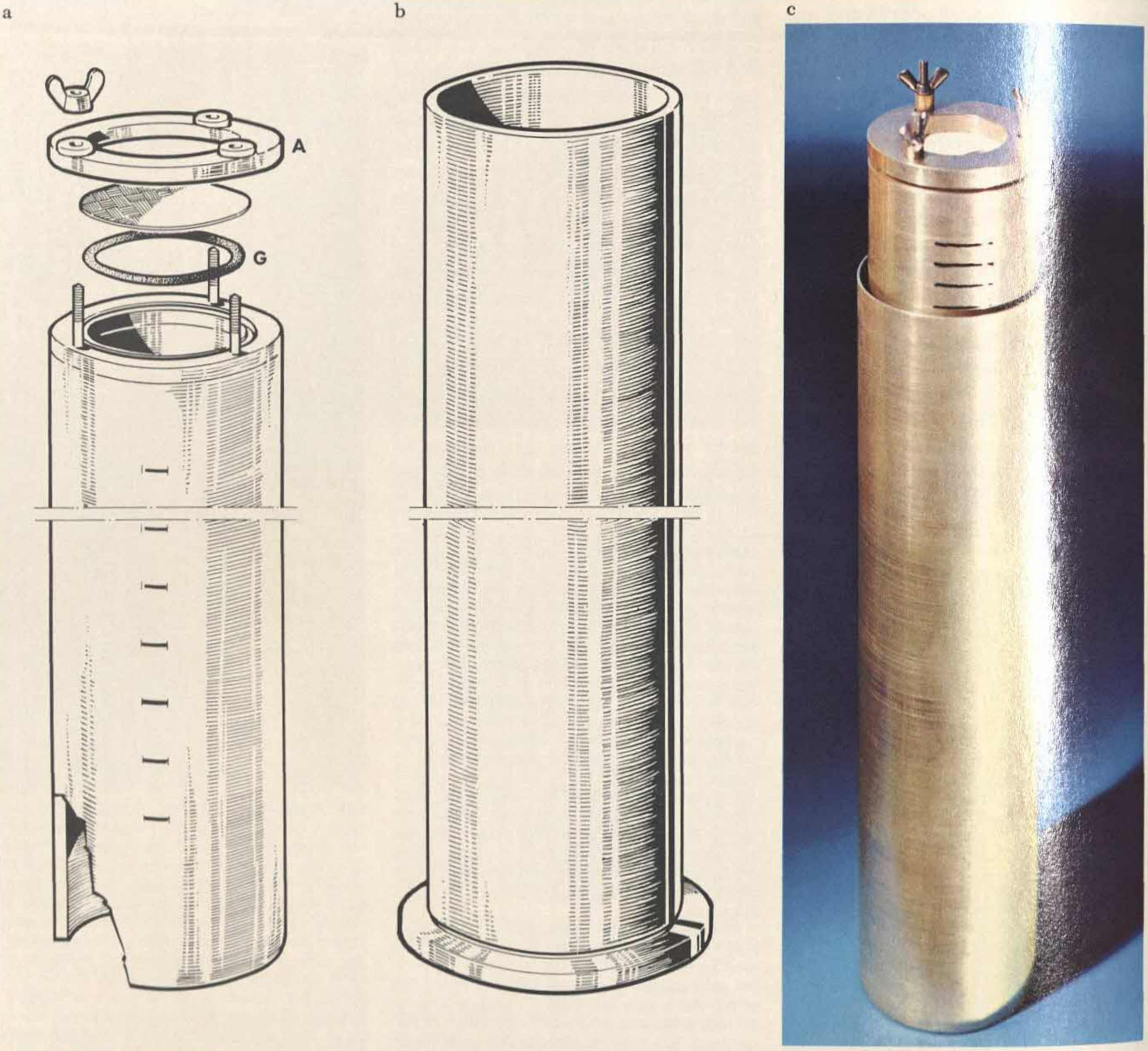

BUILDING A POROSIMETER—The most difficult part to construct is the inner cylinder. This part can be made from a brass tube having an internal diameter of 50 mm, for example, and an external diameter of 55 mm. The cylinder terminates at the top with a flange welded on as shown in Illustration 3a. The metal ring **A** is fixed to this flange by means of three bolts and wing nuts. A rubber ring **G** acts as a gasket to make the joint airtight. The sample is inserted between the metal ring and the rubber gasket. The inner cylinder must be placed inside another cylindrical container. This part can be made from a brass tube having an internal diameter of 56 mm and an external diameter of 60 mm (Illustration 3b). The inner cylinder must slide up and down inside this second cylinder without excessive friction. The time required for the inner cylinder to sink will depend on the porosity of the sample and can vary from a few seconds (in the case of thin sheets of paper) to many minutes (in the case of samples with low porosity). The second hand of an ordinary wrist watch is adequate for measuring the elapsed time. The height of the outer cylinder should be of the order of 25 cm and the inner cylinder about the same.

Illustration 3c is the complete porosimeter constructed according to these instructions. The area of the sample is 17 cm^2. In operation, the weight of the inner cylinder in this model produces an internal air pressure of 0.05 kg/cm^2. The scale on the outer face of the inner cylinder is calibrated at intervals of 10 mm. This interval corresponds to an enclosed gas volume of approximately 20 cm^3.

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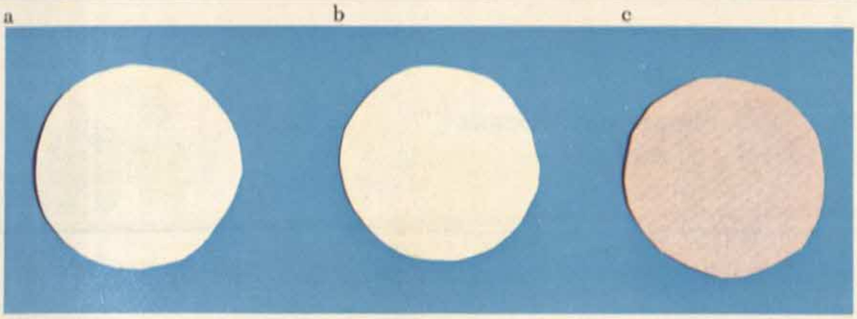

THE MEASUREMENT OF POROSITY—It is essential that the sample be held securely between the ring and the rubber gasket, airtight, to insure accuracy.

The photograph shows three samples made of paper—a piece of blotting paper (Illustration 4a), which is very porous; a piece of thin typewriting paper (Illustration 4b), and a piece of wrapping paper (Illustration 4c). These three samples have different porosities. The values decrease in the order in which the papers are listed. These porosity values with respect to air, as measured with the instrument in Illustration 3c, are found to be 2×10^{-2}, 0.5×10^{-2}, and 2×10^{-3} (cm^3/sec)•(cm/kg).

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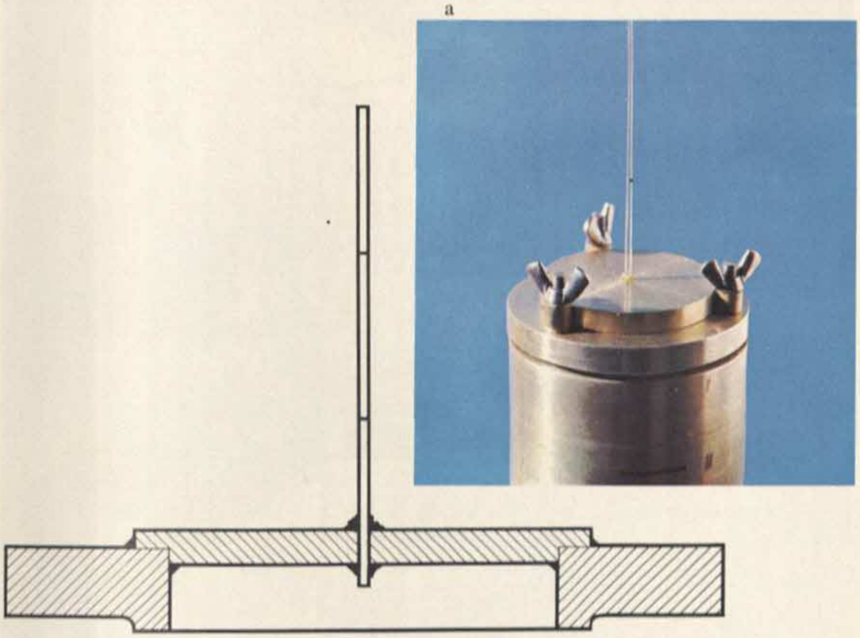
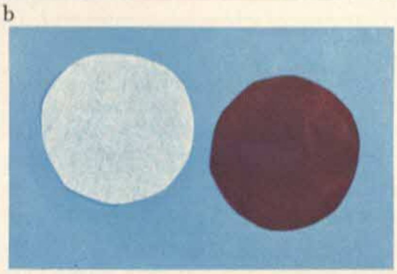




THE MICROPOROSIMETER — The instrument previously described is not adequate for measuring the porosity of substances that are only slightly porous. A simple accessory solves this problem. This accessory consists of a brass disk with a hole at the center. The disk is fastened to the metal ring that presses the sample against the rubber gasket. A capillary tube of known diameter is passed through the hole in the disk and fastened with a small amount of cement. Two notches are marked on the outside of the capillary tube (Illustration 5a). It is convenient to mark the notches 10 cm apart. Different capillary tubes may be used, provided the diameter of the tube is known.

The principle of this version of the instrument is analogous to that of the simple porosimeter. When the sample is fixed in position, the inner cylinder is introduced into the outer cylinder containing the liquid. The descent of the inner cylinder will be extremely slow, however, because the sample is only very slightly porous. It is, therefore, not very practical to wait until 20 cm^3 of gas have passed through the sample. In a relatively short time, on the other hand, a few cubic centimeters will pass through the sample. In some cases this will be as little as a fraction of a cubic centimeter. To offset the very slow rate of descent of the inner cylinder, a drop of colored liquid may be placed in the capillary tube before the inner cylinder is inserted into the outer cylinder. Because of the very small volume beneath the drop in the capillary tube, the drop will rise up the tube as air passes through the sample. The time measurement is started when the drop reaches the lower index mark, and stopped when the drop reaches the second mark. Since the volume of the capillary tube between the two marks is known, all the data needed to calculate the porosity of the sample are available. This method has been used to measure the rate of gas transmission through a sheet of paper covered with a thin film of plastic material, and a piece of oilpaper (Illustration 5b). Measurements made with this apparatus are not as accurate as those obtainable with modern professional instruments. In the first place, the effect of the friction between the walls of the two cylinders has been ignored. Furthermore, the measurements made to obtain the values inserted in the porosity formula (time of descent, surface area of the sample, volume of gas, and thickness of the sample) are all subject to errors whose magnitude depends on the accuracy with which the measurements are carried out.

glass, although the porosity of glass is minimal indeed.

Measuring the porosity of a substance is an interesting laboratory operation. As a matter of fact, it is possible to show that many substances that seem not to be porous are indeed permeable to fluids. The technique used to measure porosity is both simple and effective.

What follows is a description of an apparatus suitable for measuring the porosity of a substance to gases. This apparatus can be used for measuring high degrees of porosity and, by adding a very simple accessory, it becomes capable of measuring microporosities of the type displayed by a thin sheet of plastic.

THE SIGNIFICANCE OF POROSITY MEASUREMENTS

This experiment demonstrates that one of the most obscure properties of a solid can be explored by means of relatively simple apparatus. Very accurate measurements of porosity, such as those obtainable by the use of sophisticated instruments, are not intended here. Rather, the experiments demonstrate how to use an instrument whose accuracy depends largely on the skill of the operator.

A number of precautions that must be taken when using this apparatus must also be observed when more sophisticated instruments are being used. For example, a liquid should not be used whose vapors may dissolve or otherwise damage the porosity sample. If this should happen, the porosity characteristics of the sample would change during the course of the measurement. Sharpening laboratory techniques in tasks of this type is excellent practice for experiments that are far more difficult to carry out.

FILTERS AND ULTRAFILTERS

important selectors of particles

Filtration is used in a wide range of industrial, medical and household applications. One common example is the simple paper filter used to prepare drip coffee. The problems of filtration, and the preparation of different types of filters, are an important part of chemical research.

Filtration of coarse suspensions, or the separation of precipitates, is common in laboratory research. When a soluble salt containing insoluble impurities must be purified, it is first dissolved in water and then filtered (often with a commercially available filter material). A more difficult problem arises when the filtrate must be reduced to ash and weighed. This requires a filter material that leaves very little ash when incinerated, and that can be accurately weighed. The filtration of materials suspended in solutions that will destroy common filter materials (acids, for example) presents an even more difficult problem.

In filtering suspensions consisting of very small particles (less than 0.001 mm), or those of colloids, it is often necessary to use specially processed substances, some of which are shown in the accompanying illustrations.

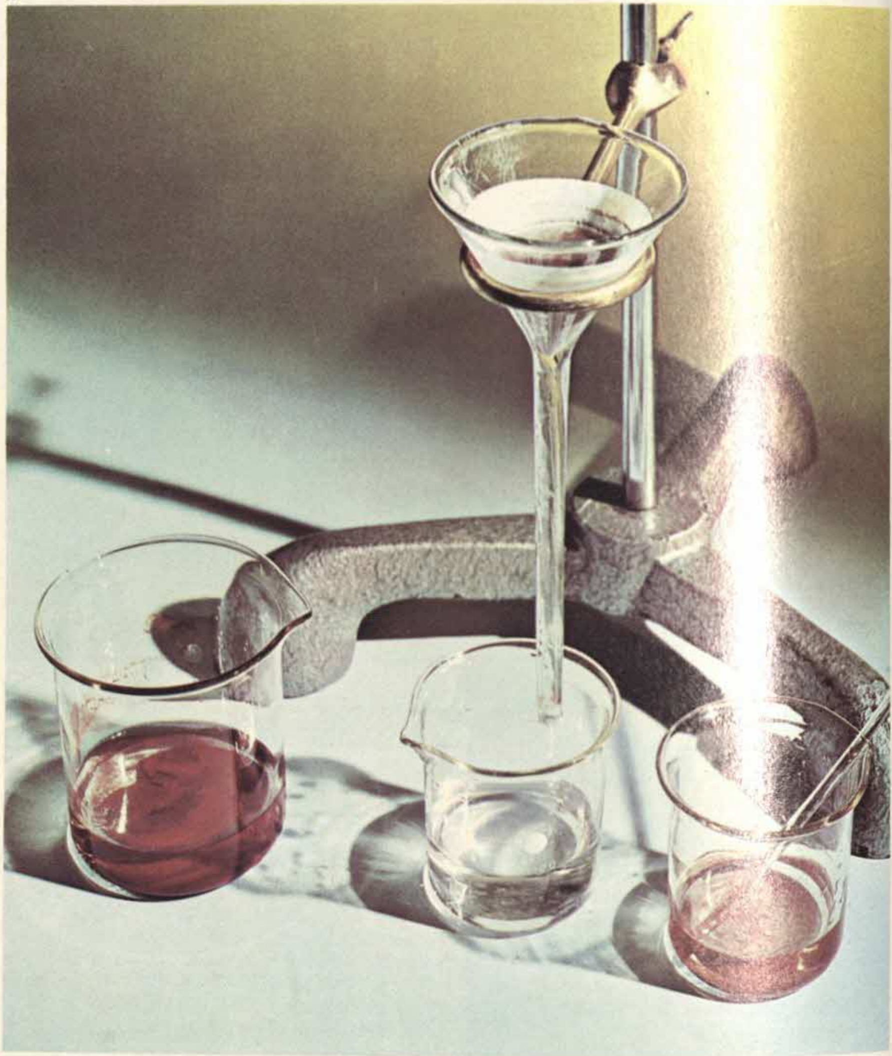
Other ultrafilters, not shown here, are obtainable commercially. The micropores are extremely regular in these filters, which can be purchased in a range of pore sizes to enable filtering particles of the desired size range. Such filters are used in brewing to remove bacteria from canned beverages and to prevent spoilage.

The basic requirements for filtration are: (1) a filter medium; (2) a fluid with suspended solids; (3) a driving force such as a pressure difference to cause the fluid to flow through the filter medium; and (4) a mechanical device to hold the filter and contain the fluid.

The driving force may be gravity, centrifugation, application of pressure on the fluid above the filter or vacuum below the filter, or a combination of several of these forces. Gravity alone may serve in the large sand-bed filters that clarify water, or in simple laboratory filtration. Most industrial filtration processes involve the use of pressure or vacuum, de-

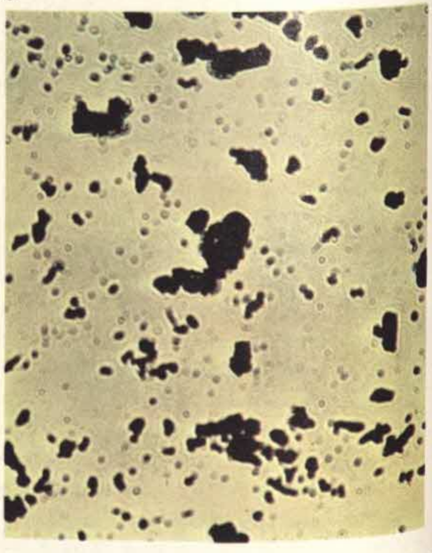
1

a



PAPER FILTERS—Most paper filters are purchased from laboratory equipment suppliers. However, paper filters cannot be used to filter particles smaller than 0.001 mm. The filters may be folded or pleated; the former method is slow because the filter rests on the funnel walls. Illustration 1a shows a suspension of very fine powder (iron oxide) being filtered. The coarser part forms a sediment, while the water is still cloudy and reddish. The filtrate is then refiltered to obtain the clear solution. By examining the substance collected on the filter paper under a microscope, it can

b

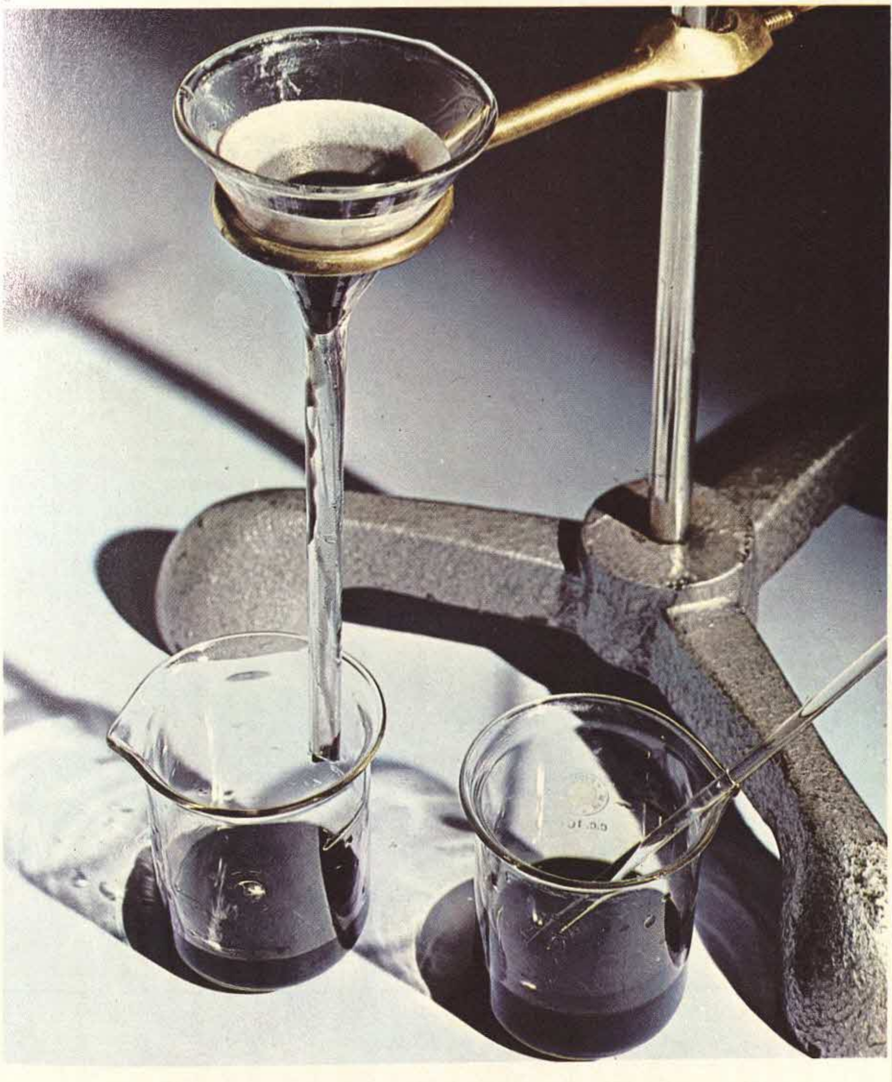


d

be seen that the iron oxide particles have been collected, and that none is less than 0.001 mm in size. Illustration 1b is a microphotograph of these particles.

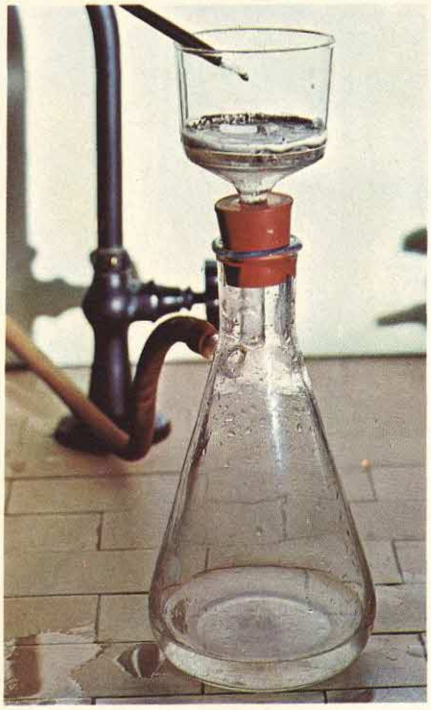
India ink is a suspension of particles that are never more than 0.001 mm; thus, India ink is a colloidal suspension. When a few drops of India ink are diluted in water and passed through a paper filter (Illustration 1c), the solution does not change color because the carbon black particles pass easily through the coarse filter. In Illustration 1d, it is impossible to distinguish the small particles of carbon black, even under high magnification.

c



COLLOID FILTERS—Colloid filters are powders that produce ultrafine filtration under special conditions. The type of powder used determines the speed and effectiveness of the filtration process. To accelerate the process, a vacuum is created in the flask. The filter shown is kaolin powder, which expands in water to form colloidal suspensions. The kaolin is dampened and a layer spread over a paper filter. The suspension to be filtered is placed on the filter by a dropper or some other device, without disturbing the kaolin. The process is slow, but will completely filter such a colloid as India ink.

2



pending on the type of filter used, to increase the rate of filtration and also to decrease the size of the equipment needed.

Gravity sand-bed installations in city water plants filter more gallons of fluid than any other type. They are usually concrete tanks with a grating at the bottom. Above the grating are graded layers of crushed rock and fine sand. After solids accumulate, the bed may be backwashed and cleaned with clear water.

In industry, crushed coke in lead-lined boxes is used to filter sulfuric acid and crushed limestone is used to filter alkaline solutions. Organic solutions may be filtered through beds of charcoal.

An example of a pressure-vacuum filter system is found in the household vacuum sweeper, where dirt is retained inside a cloth or paper bag. Another example is the oil filter cartridge inside an automobile engine.

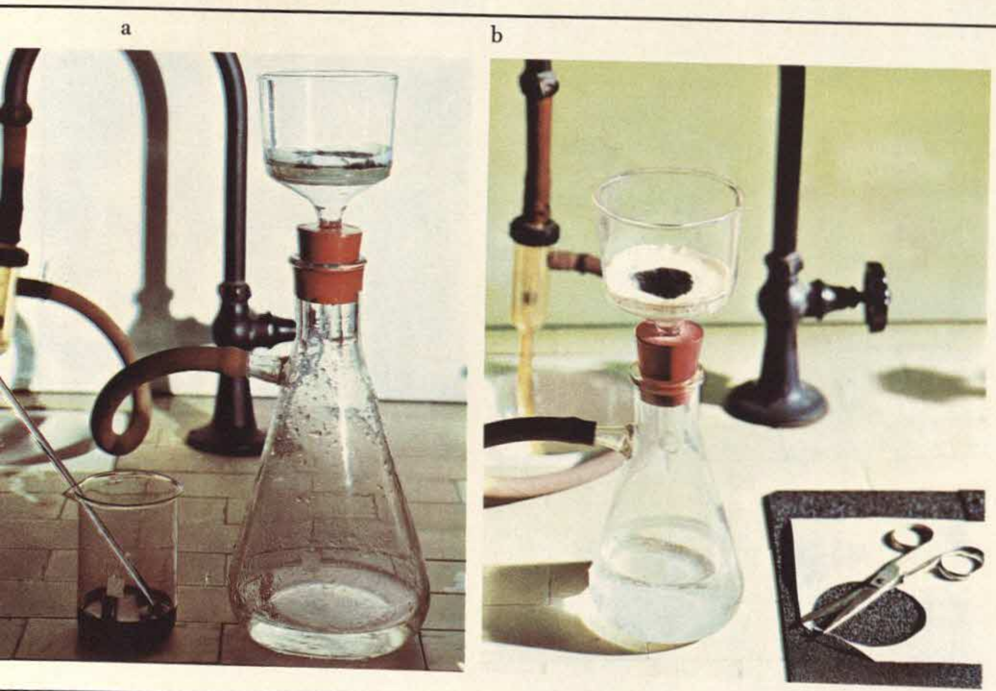
In some filtration processes the desired product is the clarified fluid; in others it is the solid or filtrate removed from the fluid. In still others, both clarified fluid and solid are recovered and put to use.

3

PREPARATION OF ULTRAFILTERS—The kaolin filter effectively retains suspended particles of from 0.0001 to 0.00001 mm in size. An even more effective filter is required, however, to retain smaller colloidal particles. Nitrocellulose membranes are commonly used as ultrafilters by dissolving them in a mixture of alcohol and ether, and using this solution to soak coarser filters. To make a nitrocellulose filter, a drop of the solution is placed in still water where it spreads to form a membrane when the solvent evaporates.

This membrane has extremely small pores. The membrane has the disadvantage of being extremely delicate, however, and must be supported by filter paper, which will not break it. In laboratory tests, the membrane can be checked with a suspension of India ink, which will reveal even the slightest leak of suspended particles. In Illustration 3a, a sheet of filter paper is being soaked in nitrocellulose to make an ultrafilter. The film must be used before the solvent (ether and alcohol) evaporates, and the small amount of water in the alcohol (5 percent) must remain in the nitrocellulose. Illustration 3b shows a solution of India ink both before and after ultrafiltration.

4



PARCHMENT FILTERS—An intermediate type of filter can be made from parchment, which acts as an ultrafilter to retain some colloidal particles. Common tracing paper sealed to the edges of coarse filter paper will filter India ink under vacuum (Illustration 4a). A more efficient filter can be prepared from vegetable parchment similar to that used for mechanical drawing, and dampened to fit into the funnel (Illustration 4b).

ORGANIC CHEMISTRY AND METHANE

the boundless horizons of the chemistry of carbon

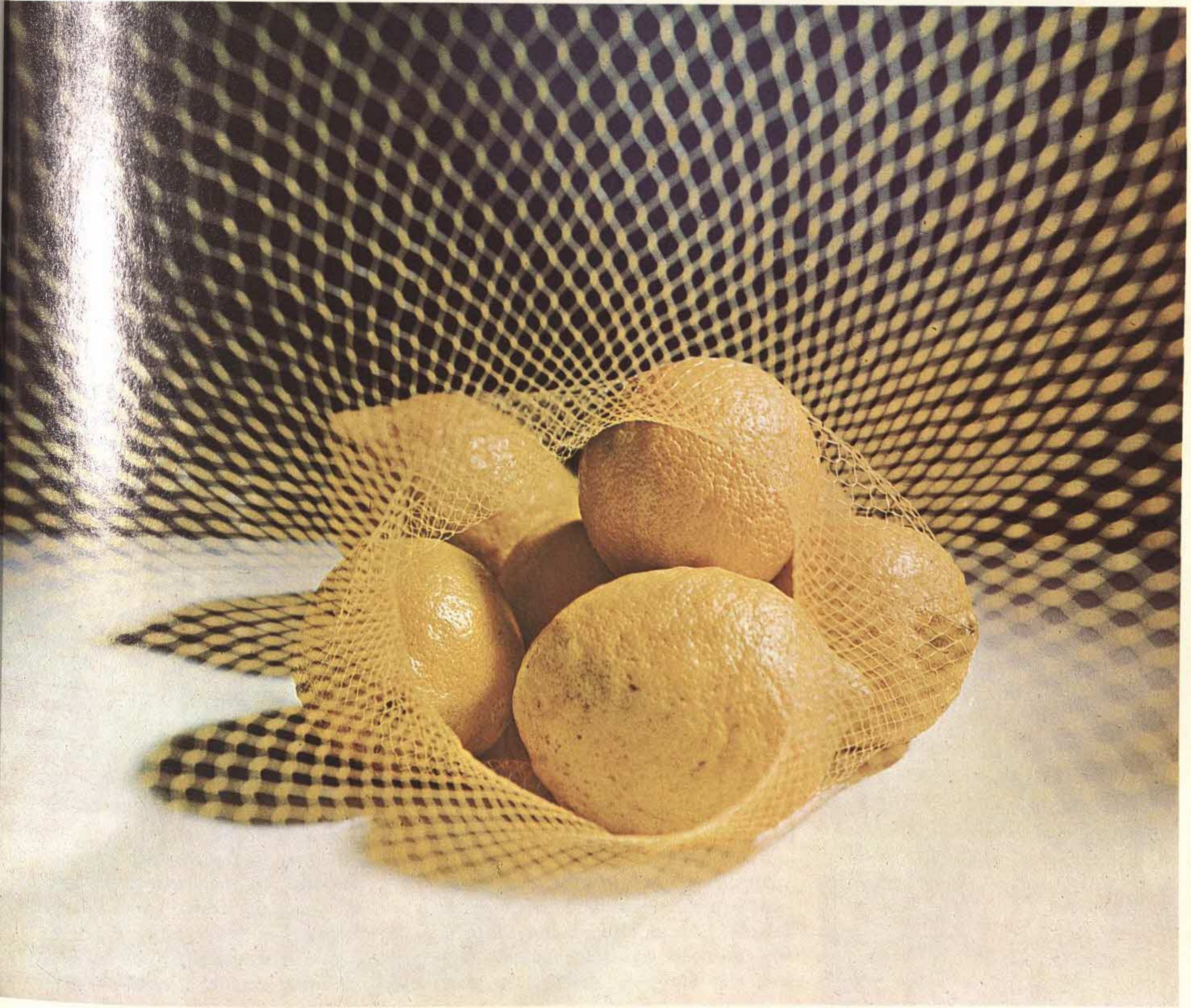
The discovery that inorganic substances could be made to yield organic ones was first made in 1828 by the German chemist Friedrich Wöhler. This discovery marked the beginning of modern organic chemistry. Previously, it had been thought that all organic substances contained a vital "life force" and that artificial synthesis was impossible. Left unexplained was the fact that organic compounds gave off inorganic substances (water and carbon dioxide) when burned.

Many organic substances have been known to man since the days of alchemy. These same substances are common to all living organisms and appear in many forms (solids, liquids, or gases). In addition, they are used in vital processes in the manufacture of textiles, drugs, petroleum, plastics, and various foodstuffs.

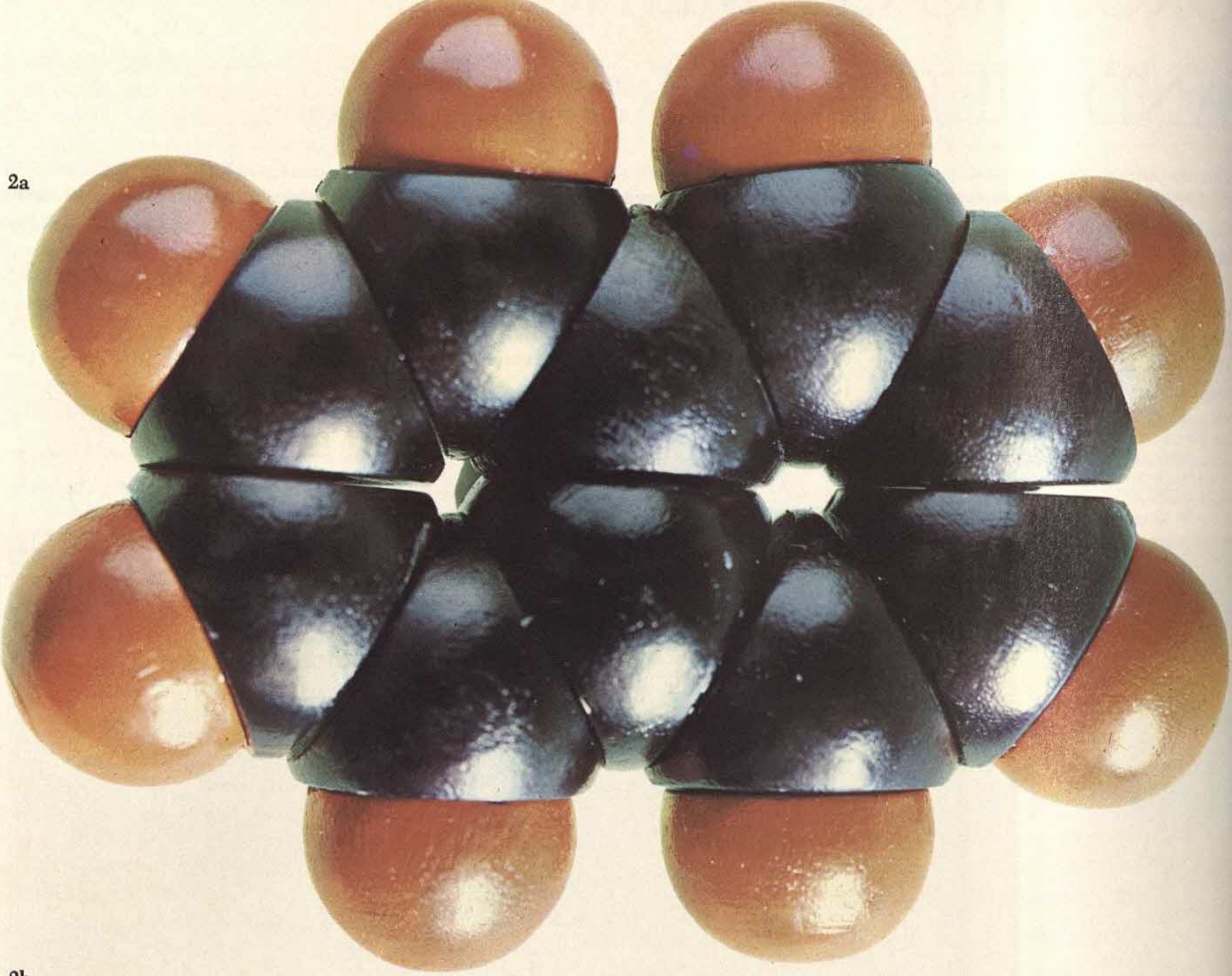
Organic chemistry, or the study of carbon compounds, thus developed along two lines—the investigation of natural organic substances, and the laboratory preparation of completely new organic compounds. How many of these compounds are known? It is impossible to answer this question because new ones are discovered every day.

The seemingly endless number of car-

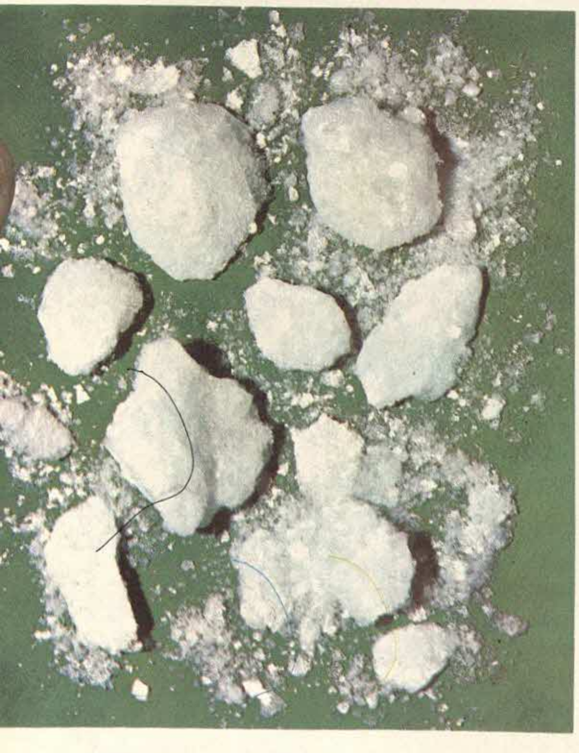
WONDERS OF ORGANIC CHEMISTRY—These lemons are shown in a bag made from plastic netting, which was synthesized from petroleum—a common example of natural and synthetic substances that coexist in organic chemistry. Synthetics are constantly put to new uses.



2a



2b



NAPHTHALENE — This aromatic hydrocarbon is shown as a conglomerate in the compact model of a molecule (Illustration 2a), and as small and shiny crystals in its natural form (Illustration 2b). It is widely used in the manufacture of dyes and synthetic resins.

bon compounds stems from the fact that the atoms in carbon compounds are linked to each other by bonds that are so stable that many can exist simultaneously in a single molecule; in theory, there is no limit to the number of carbon atoms that can be linked together in the same molecule. Few, if any, of the inorganic elements possess this property, which is why they can be studied together. Boron, silicon, and nitrogen are the nearest to carbon in the periodic table, but they possess this property only to a slight degree.

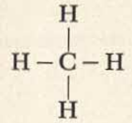
A molecule is termed organic when its basic structure consists of carbon atoms; however, it can also contain atoms of other elements, especially hydrogen, oxygen, and nitrogen. Moreover, a given number of carbon atoms may be arranged in different configurations to form separate molecules (isomerism). Carbon atoms also may be linked by single, double, or even triple bonds.

Generally, carbon compounds decompose when heated (some are stable only at sub-zero temperatures), but a few resist even very high temperatures. Some behave like bases, others act like acids, and still others are neutral. They may exist in different physical forms (solids, liquids, or gases) and colors.

In his letter to the Swedish chemist J. J. Berzelius, Wöhler excitedly told of heating ammonium cyanate and obtaining urea, a well-known organic substance. This discovery led to the eventual synthesis of many organic compounds, and to advances in medicine, agriculture, and industry.

METHANE

The most common type of chemical bond in organic chemistry is the covalent bond in which two electrons are shared by two atoms. Each carbon atom is tetravalent, so that four electrons can form bonds with other, separate atoms. Methane, or common marsh gas, is a good example of this type of bond. A single carbon atom is linked to four hydrogen atoms. In this arrangement, the hydrogen atoms are monovalent and have only one electron that can be linked to other atoms, so that four atoms are needed to occupy the four carbon electrons. Organic chemists usually indicate such simple bonds by a dash; the methane molecule is written as:



$$\begin{array}{c} H \\ | \\ H-C-H \\ | \\ H \end{array}$$

This representation, although accurate, does not indicate the true spatial arrangement of the methane molecule or its inherent stability. Generally, a molecule is considered stable when there are two electrons around each atom of hydrogen and eight more in the outer stratum of the other atoms. Methane fulfills this condition $(2 \times 4 = 8)$.

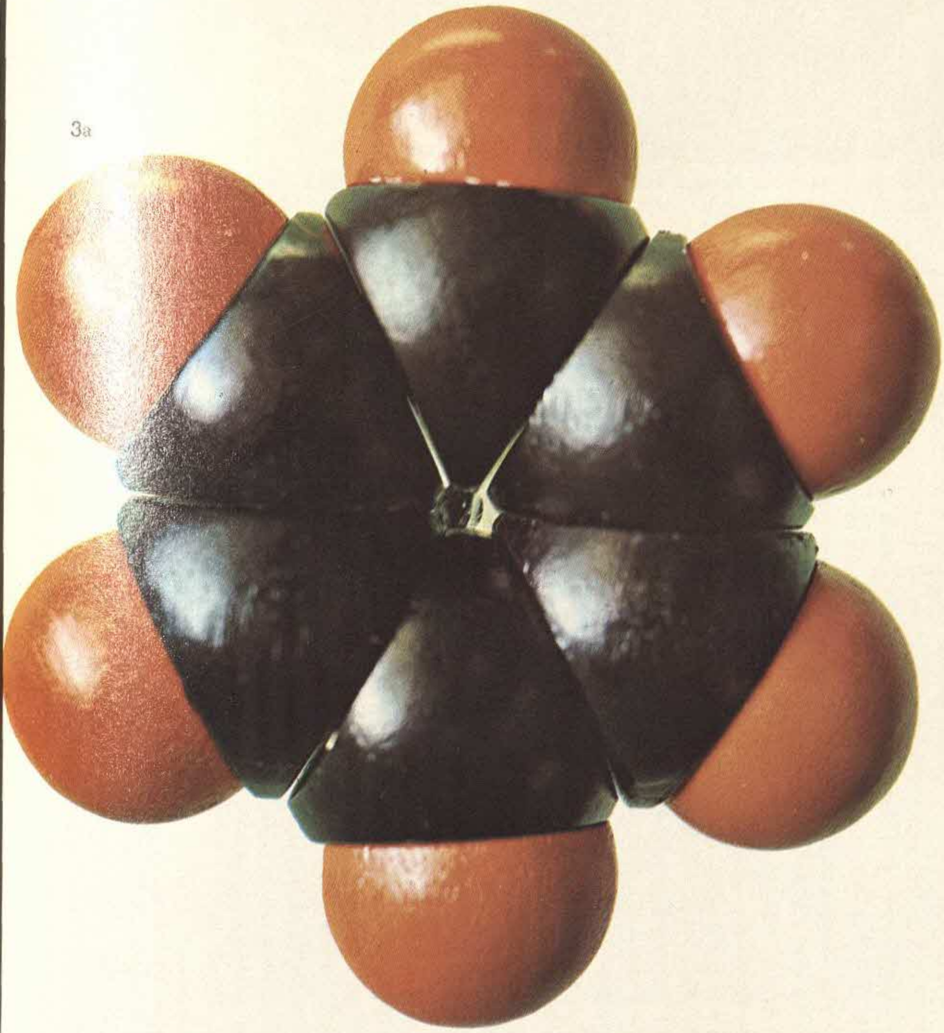
In methane, each molecule has a carbon atom linked to four hydrogen atoms by means of four covalent bonds. The carbon atom is, therefore, in the center of a regular tetrahedron, and the four bonds are directed toward the vertices. Thus, the methane molecule is perfectly symmetrical.

METHANE IN NATURE

The principal component of many natural gases, methane is formed when plant cellulose ferments due to the action of microorganisms either underground or in stagnant water. Common marsh gas is the best-known example, and is visible as bubbles in stagnant pools. Methane also develops in the oxygen-poor environment of coal mines where it mixes with air to form the dangerously explosive mixture known as firedamp.

Methane is colorless and practically odorless (any actual odor is probably caused by impurities) and is lighter than air. It burns with a very hot flame and is widely used as a fuel (compressed gas). Experiments conducted by the American chemists Harold Urey and Stanley Miller demonstrated that a mixture of methane, water, ammonia, and hydrogen could be transformed, through an electrical discharge, into amino acids, the main constituent of proteins. In time this reaction may prove the theory that life originated with a "big bang" in the presence of gases.

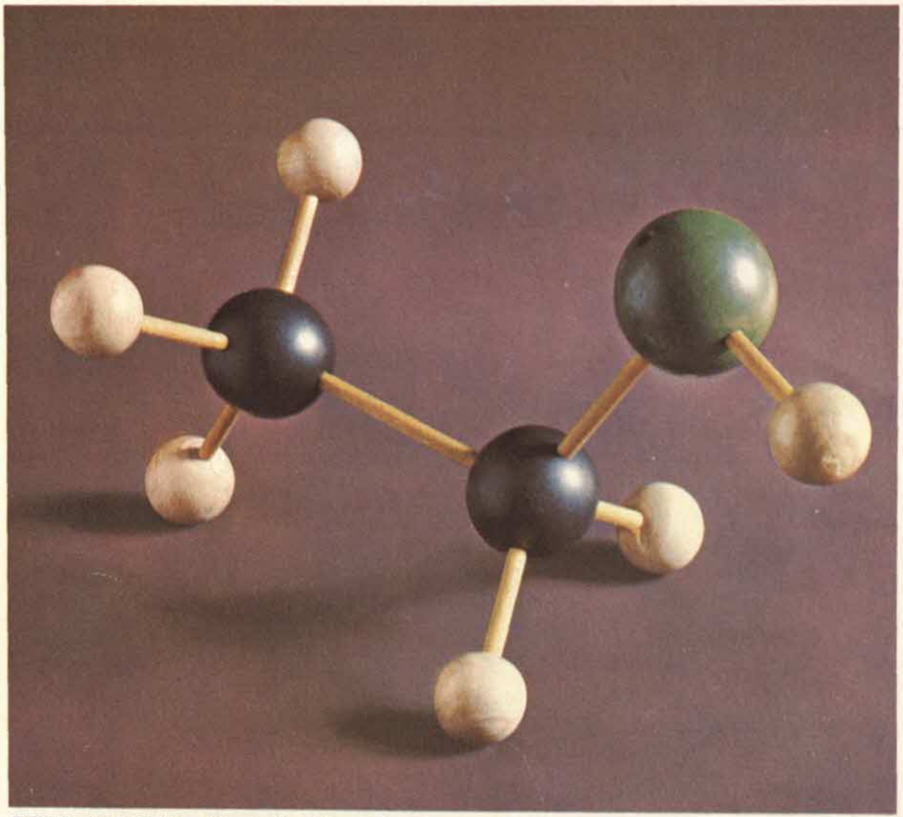
3a



BENZENE—The benzene molecule in Illustration 3a has the typical hexagonal structure of aromatic organic substances. It is a colorless and quite refractive liquid (Illustration 3b).

3b

4a

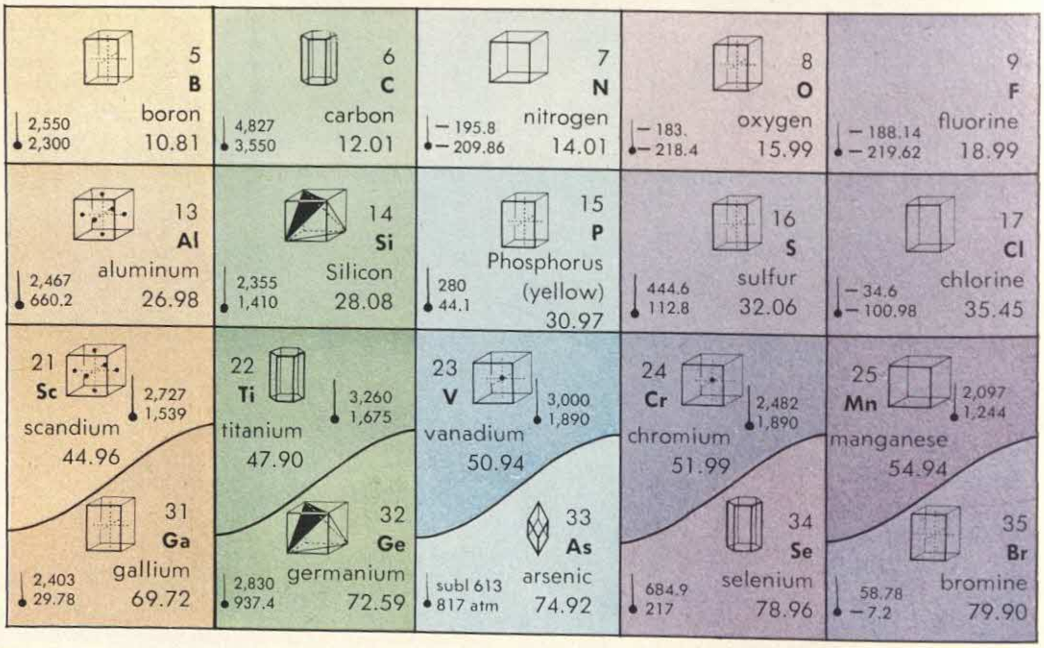


4b

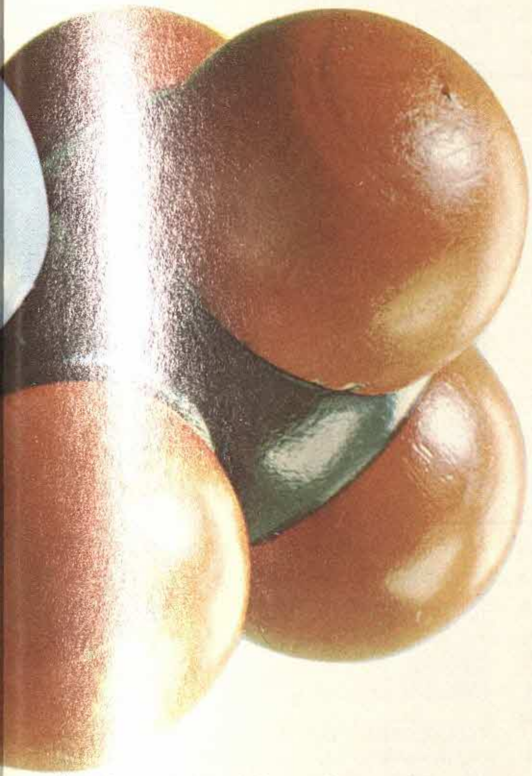
ETHYL ALCOHOL—All of the bonds in an ethyl alcohol molecule are shown in this model (Illustration 4a). The largest atom is that of oxygen (green), which is linked to both a carbon atom (black) and a hydrogen atom (white). The second, compact model in Illustra-

OTHER "ORGANIC" ELEMENTS—Silicon, boron, and nitrogen are near carbon in the periodic table and show some tendency to form similar chains. The electron structure of these elements makes this slight similarity possible. The pairs of numbers at the lower left of each box are the boiling point and the melting point respectively in degrees C.

5



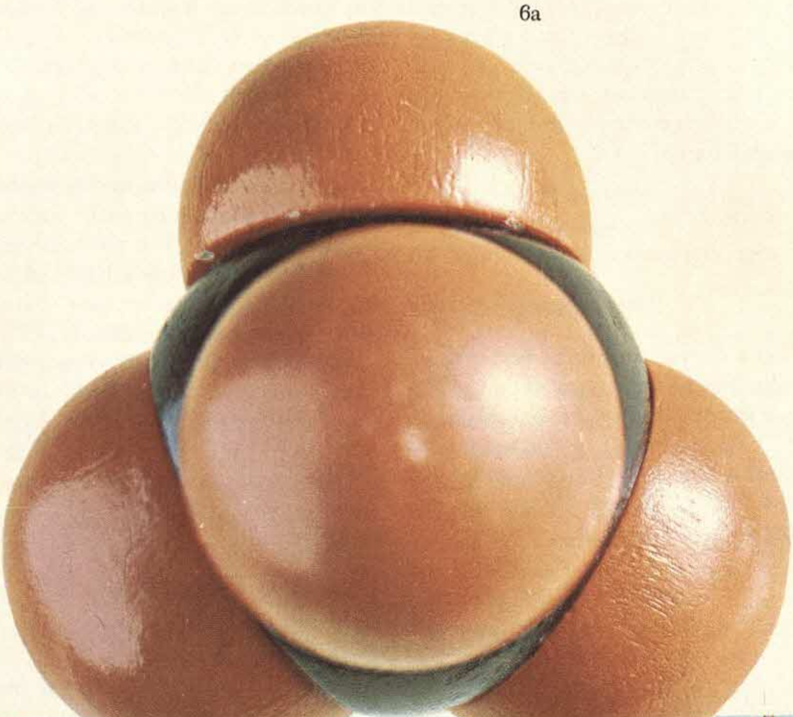
5 **B** boron 2,550 2,300 10.81	6 **C** carbon 4,827 3,550 12.01	7 **N** nitrogen −195.8 −209.86 14.01	8 **O** oxygen −183. −218.4 15.99	9 **F** fluorine −188.14 −219.62 18.99
13 **Al** aluminum 2,467 660.2 26.98	14 **Si** Silicon 2,355 1,410 28.08	15 **P** Phosphorus (yellow) 280 44.1 30.97	16 **S** sulfur 444.6 112.8 32.06	17 **Cl** chlorine −34.6 −100.98 35.45
21 **Sc** 2,727 1,539 scandium 44.96	22 **Ti** 3,260 1,675 titanium 47.90	23 **V** 3,000 1,890 vanadium 50.94	24 **Cr** 2,482 1,890 chromium 51.99	25 **Mn** 2,097 1,244 manganese 54.94
31 **Ga** gallium 2,403 29.78 69.72	32 **Ge** germanium 2,830 937.4 72.59	33 **As** arsenic subl 613 817 atm 74.92	34 **Se** selenium 684.9 217 78.96	35 **Br** bromine 58.78 −7.2 79.90



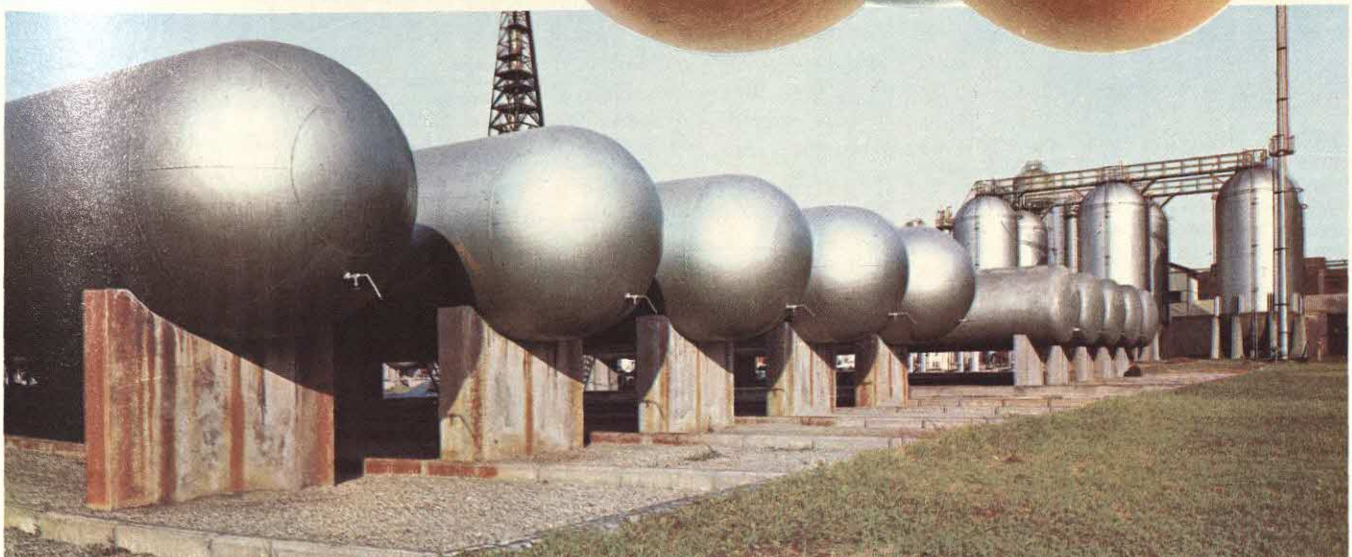
tion 4b shows the minimum distance that actually separates these atoms from one another.

METHANE—The simplest of hydrocarbons has a perfectly symmetrical structure as this compact model (Illustration 6a) shows. The huge storage tanks in Illustration 6b contain methane in the gaseous state and under pressure.

6a



6b

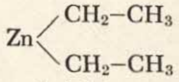


THE ORGANOMETALLIC COMPOUNDS

fundamental components in making polymers

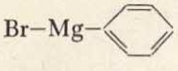
Because of their extreme reactivity and pronounced catalytic properties, the organometallic compounds have been the subject of rapid research and development in recent years. In fact, some metal-organic derivatives are responsible for industrial applications unknown only a short time ago. Alkyl aluminum compounds are examples of such substances.

Organometallic compounds comprise a series in which a direct bond occurs between a metallic atom and a carbon atom. Two such compounds are diethyl zinc and phenylmagnesium bromide, whose structural formulas are:



$$Zn\begin{cases}CH_2-CH_3\\CH_2-CH_3\end{cases}$$

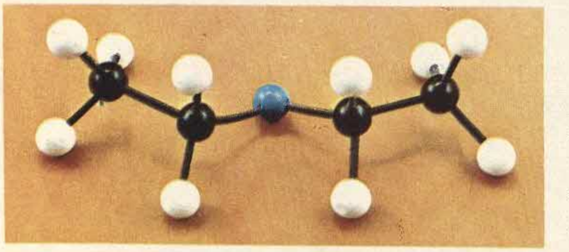
diethyl zinc



phenylmagnesium bromide

Diethyl zinc was among the first organometallic compounds prepared by the English chemist Sir Edward Frankland in 1850. This pioneering work led to his appointment as professor of chemistry at Owens College in Manchester the following year.

1

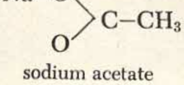


DIETHYL ZINC—This model represents the structure of the first organometallic compound to be prepared (Frankland, 1850). Diethyl zinc can be used in many reactions because it is less reactive than the Grignard reagent ethylmagnesium iodide.

Simply because a metal atom is contained in an organic molecule does not necessarily classify the molecule as organometallic. For example, both sodium methylate and sodium acetate contain a metallic atom, but it is not bonded directly to a carbon atom:

$Na-O-CH_3$

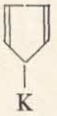
sodium methylate



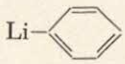
$$\begin{matrix}Na-O\\O\end{matrix}\!\!>C-CH_3$$

sodium acetate

The organic radical to which the metallic atom is bound can be a member of any organic series (alkyl, cycloalkyl, alkenyl, alkynyl, aryl, and so forth):



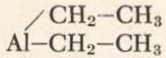
cyclopentadienyl potassium



phenyl lithium

$Na-CH_2-CH=CH_2$

allyl sodium



$$Al\begin{cases}CH_2-CH_3\\CH_2-CH_3\\CH_2-CH_3\end{cases}$$

triethyl aluminum

Thus, it is easily understood just how vast the number of organometallic compounds is, especially when it is remembered that the elements with some degree of metallic character represent more than two thirds of the natural elements.

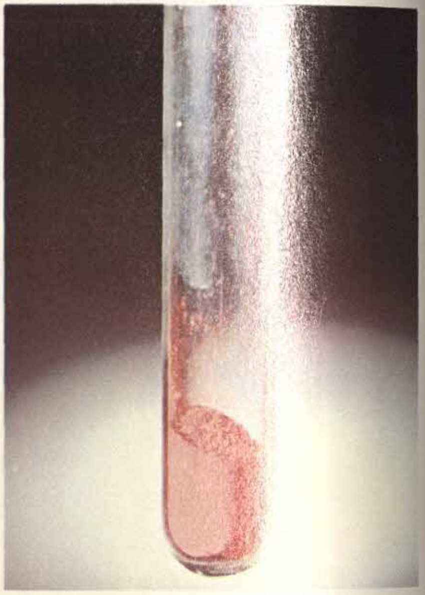
The metalloids (boron, germanium, silicon, selenium, arsenic, and so forth) also form organic derivatives. However, since they exhibit properties somewhat different from those of true organometallic compounds, they represent a special class.

GENERAL PROPERTIES AND REACTIVITY

The preparation and handling of organometallic compounds often requires special precautions. For example, it may be necessary to carry out various operations in an inert atmosphere. Pure, dry nitrogen, for example, precludes the detrimental action of atmospheric oxygen and water vapor on most organometallics, even in minute concentrations. Of course, just as with all classes of compounds, there are different degrees of reactivities among the members. Compounds like butyl lithium ($Li-C_4H_9$) and methyl sodium ($Na-CH_3$) represent highly reactive materials that are pyrophoric; that is, they react instantly with water and burst spontaneously into flame in air. On the other hand, the organic derivatives of heavy metals such as diethyl mercury, $Hg(C_2H_5)_2$ exhibit considerably less reactivity, reacting neither with water nor alcohols, and are unable to rupture double bonds.

In general, the reactivity of organometallic compounds is related to the degree of polarity of the carbon-metal bond.

2



TITANOCENE—This red powder is a mixed organometallic compound with the formula $(C_5H_5)_2TiCl_2$. It does not react with atmospheric oxygen or water vapor, and is soluble in the hydrocarbon solvents. When mixed with triethyl aluminum, titanocene forms yet another soluble compound, blue in color, that is used as a catalyst in the polymerization of ethylene.

It has been observed that reactivity is greater when this polarity is more pronounced.

For the sake of clarification, it is necessary to understand the concept of polarity and nonpolarity in covalent bonds. In the organic compounds, the pair of bond electrons is arranged symmetrically only when the atoms are identical, as

$$C : C \qquad O : O$$

apolar covalent bonds

In all other cases, the greater part of the electron pair will belong to the more electronegative atom, thus creating a fractional charge (represented by $\delta\pm$) in all the atoms:

$$\underset{\delta+}{C}\;:\underset{\delta-}{Cl} \qquad \underset{\delta-}{C}:\;\underset{\delta+}{Na}$$

polar covalent bonds

The carbon atom represents the electronegative part of an organometallic compound while the electropositive nature of the metal atom tends to repel electrons.

Naturally, the more electropositive the metal, the greater the polarity of its bond with carbon. The limit to this polarity occurs, however, when the bond ceases to be covalent and becomes ionic. In an instance such as $^{-}C : M^{+}$, the two atoms acquire a unit charge.

The alkali metals, because they are electropositive, form covalent bonds with a high degree of polarity. On the opposite end of the scale are the heavy metals (mercury and lead, for example) that tend to form bonds of low polarity. With regard to the alkali metals, it is interesting to note that their combination with certain organic groups results in an essentially ionic bond, as exemplified by sodium acetylide, $CH{\equiv}C\ :^{-}\ Na^{+}$.

Certain physical properties also depend on the nature of the carbon-metal bond. For example, the organometallic compounds with low polarity are less volatile and more soluble in hydrocarbon solvents than are highly polar compounds.

The accompanying table illustrates the reactivity and some physical properties of several important organometallic compounds. These compounds are listed in decreasing order of metal electropositivity. The letters A, B, and C represent the relative degree of reactivity, A indicating highly reactive, B moderately active, and C relatively inactive.

COMPOUND	IONIC CHARACTER OF C – M BOND, IN % IONIZATION	PHYSICAL CHARACTERISTICS AND STABILITY	REACTIVITY
$NaCH_3$ methyl sodium	47	unstable when heated	A
$LiCH_3$ methyl lithium	43	unstable when heated	A
LiC_4H_9 butyl lithium	—	liquid, very slightly soluble	A
$Mg(CH_3)_2$ dimethyl magnesium	34	slightly volatile at high temperatures	B
$BrMgCH_3$ methylmagnesium bromide	—	solid, non-volatile	B
$Be(C_2H_5)_2$ diethyl beryllium	20	volatile	B
$Zn(C_2H_5)_2$ diethyl zinc	18	liquid, boiling point 118° C	B
$Cd(CH_3)_2$ dimethyl cadmium	15	liquid, boiling point 105° C	B
$Pb(C_2H_5)_4$ tetraethyl lead	12	liquid, boiling point 202° C	C
$Hg(CH_3)_2$ dimethyl mercury	9	liquid, boiling point 92° C	C

Those compounds listed as highly reactive lend themselves to use in the following reactions: addition to the olefinic double bond, hydrolysis and oxygenation (reactions that are frequently violent), and procedures involving carbon dioxide, alcohols, acids, and carbonyl compounds.

Moderately active compounds cannot be added to the olefinic double bonds, nor do they react easily with carbon dioxide. On the other hand, such compounds can readily be added to $>C{=}O$ groups, and will react with water, oxygen, and acids.

The relatively inactive substances react with acids, but show a marked resistance to other types of reactions.

Some of these reactions can be examined in detail by referring to a pair of compounds often used in laboratory synthesis: butyl lithium and ethylmagnesium bromide. The reaction mechanisms are typical of organometallic compounds, and are based on an electropositive agent reacting with the carbon atom in the carbon-metal bond. The general effect of the organometallics is to produce both a reduction and an alkylation.

PREPARATION OF ORGANOMETALLIC COMPOUNDS

A commonly used synthesis is that of the reaction between an organic halide and an active metal; for example:

$$\underset{\substack{\text{butyl}\\\text{bromide}}}{C_4H_9Br} + 2Li \longrightarrow \underset{\substack{\text{butyl}\\\text{lithium}}}{C_4H_9Li} + LiBr$$

$$\underset{\substack{\text{ethyl}\\\text{iodide}}}{C_2H_5I} + Mg \longrightarrow \underset{\substack{\text{ethylmag-}\\\text{nesium iodide}}}{C_2H_5MgI}$$

Lithium, magnesium, and zinc are particularly suitable for use in such reactions, magnesium in the form of shavings, lithium and zinc in finely divided states. The reactions are usually carried out in a solvent such as ether that is capable of dissolving both the starting halide and the resulting compound. Furthermore, the reaction must be performed in an atmosphere devoid of oxygen.

The order of reactivity of the halides should be noted, especially since the fluorides do not react with lithium, magnesium, or zinc: iodide > bromide > chloride.

Another type of synthesis consists of the exchange between a metal and an organometallic compound:

$$2Na + \underset{\substack{\text{dimethyl}\\\text{mercury}}}{Hg(CH_3)_2} \longrightarrow \underset{\substack{\text{methyl}\\\text{sodium}}}{2NaCH_3} + Hg$$

In this typical case, the more electropositive metal effects the displacement. The consequence is that the organometallic product will be more reactive than that from which it was formed.

A third fundamental synthesis is the reaction between a metallic halide and an organometallic compound:

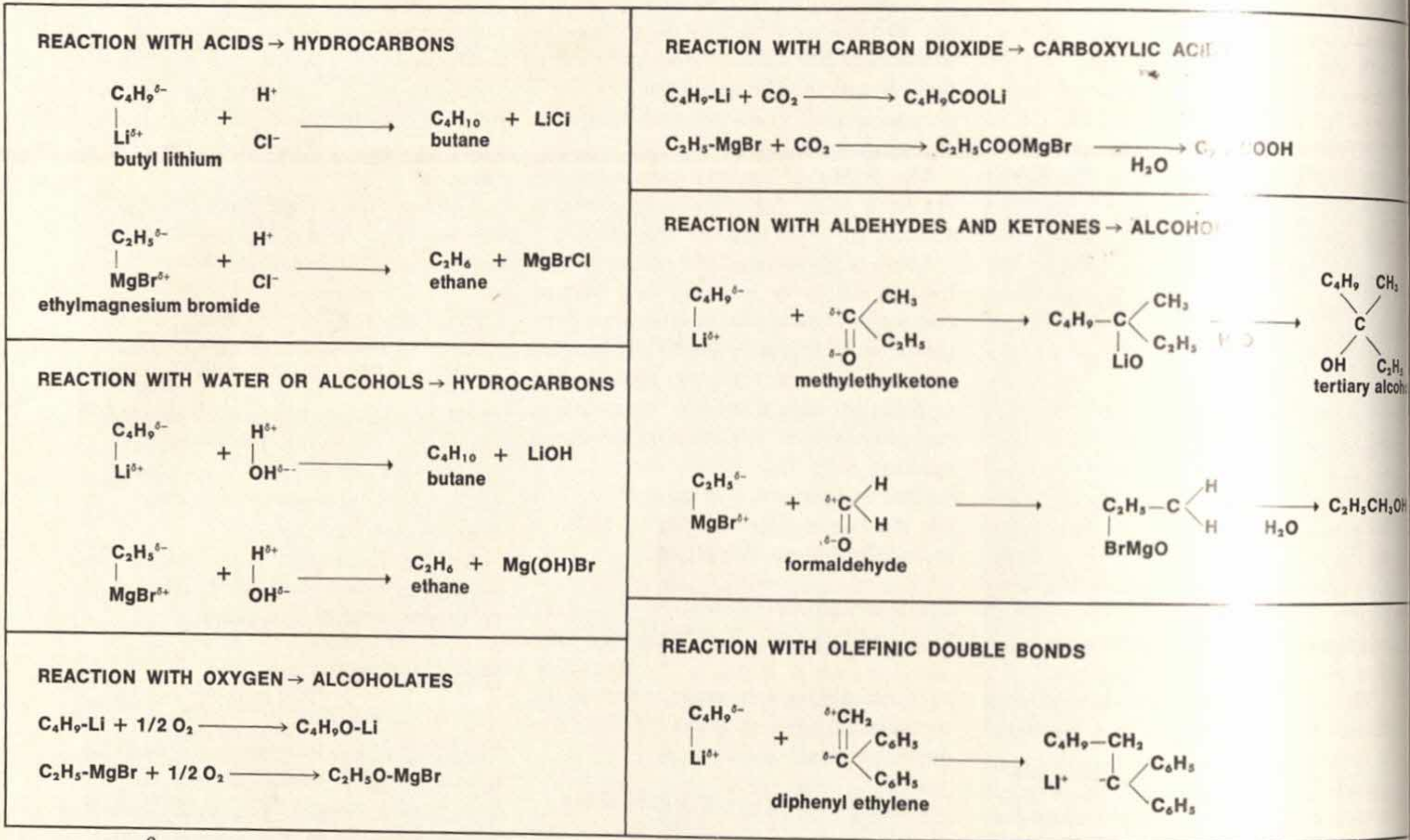
$$HgCl_2 + 2C_2H_5MgCl \longrightarrow Hg(C_2H_5)_2 + 2MgCl_2.$$

The metal of the reacting halide must be less electropositive than that in the organometallic reagent. The result, here, is the formation of an organometallic product less reactive than the reactant counterpart. This synthesis gives the opposite result of that involving a metal and an organometallic compound.

The second and third reactions described above allow the preparation of a wide variety of organometallic substances from the lithium alkyls and the alkylmagnesium halides. In turn, these materials are easily produced in the reaction between an organic halide and an active metal.

APPLICATIONS OF THE ORGANOMETALLIC COMPOUNDS

Although many organometallic compounds have been known for some time, especially the important alkyl and arylmagnesium halides known as Grignard reagents, their usefulness as catalysts in oxidation, hydrogenation, and polymerization reactions has only recently been exploited. For example, the alkyl and aryl compounds of sodium and lithium are prepared (in the case of sodium alkyls) by the action of sodium metal on a mercury alkyl or zinc alkyl; lithium alkyls and aryls have been prepared from lithium metal and alkyl and aryl halides. Alkyl and aryl sodium and lithium compounds are now widely used as initiators



REACTION WITH ACIDS → HYDROCARBONS

$C_4H_9^{\delta-}\text{—}Li^{\delta+} + H^+Cl^- \longrightarrow C_4H_{10} + LiCl$

butyl lithium; butane

$C_2H_5^{\delta-}\text{—}MgBr^{\delta+} + H^+Cl^- \longrightarrow C_2H_6 + MgBrCl$

ethylmagnesium bromide; ethane

REACTION WITH WATER OR ALCOHOLS → HYDROCARBONS

$C_4H_9^{\delta-}\text{—}Li^{\delta+} + H^{\delta+}\text{—}OH^{\delta-} \longrightarrow C_4H_{10} + LiOH$

butane

$C_2H_5^{\delta-}\text{—}MgBr^{\delta+} + H^{\delta+}\text{—}OH^{\delta-} \longrightarrow C_2H_6 + Mg(OH)Br$

ethane

REACTION WITH OXYGEN → ALCOHOLATES

$C_4H_9\text{-}Li + 1/2\ O_2 \longrightarrow C_4H_9O\text{-}Li$

$C_2H_5\text{-}MgBr + 1/2\ O_2 \longrightarrow C_2H_5O\text{-}MgBr$

REACTION WITH CARBON DIOXIDE → CARBOXYLIC ACI

$C_4H_9\text{-}Li + CO_2 \longrightarrow C_4H_9COOLi$

$C_2H_5\text{-}MgBr + CO_2 \longrightarrow C_2H_5COOMgBr \xrightarrow[H_2O]{} C\ \ OOH$

REACTION WITH ALDEHYDES AND KETONES → ALCOHO

$C_4H_9^{\delta-}\text{—}Li^{\delta+} + {}^{\delta+}C(={}^{\delta-}O)(CH_3)(C_2H_5) \longrightarrow C_4H_9\text{—}C(CH_3)(C_2H_5)(LiO) \longrightarrow C(C_4H_9)(CH_3)(OH)(C_2H_5)$

methylethylketone; tertiary alcoh

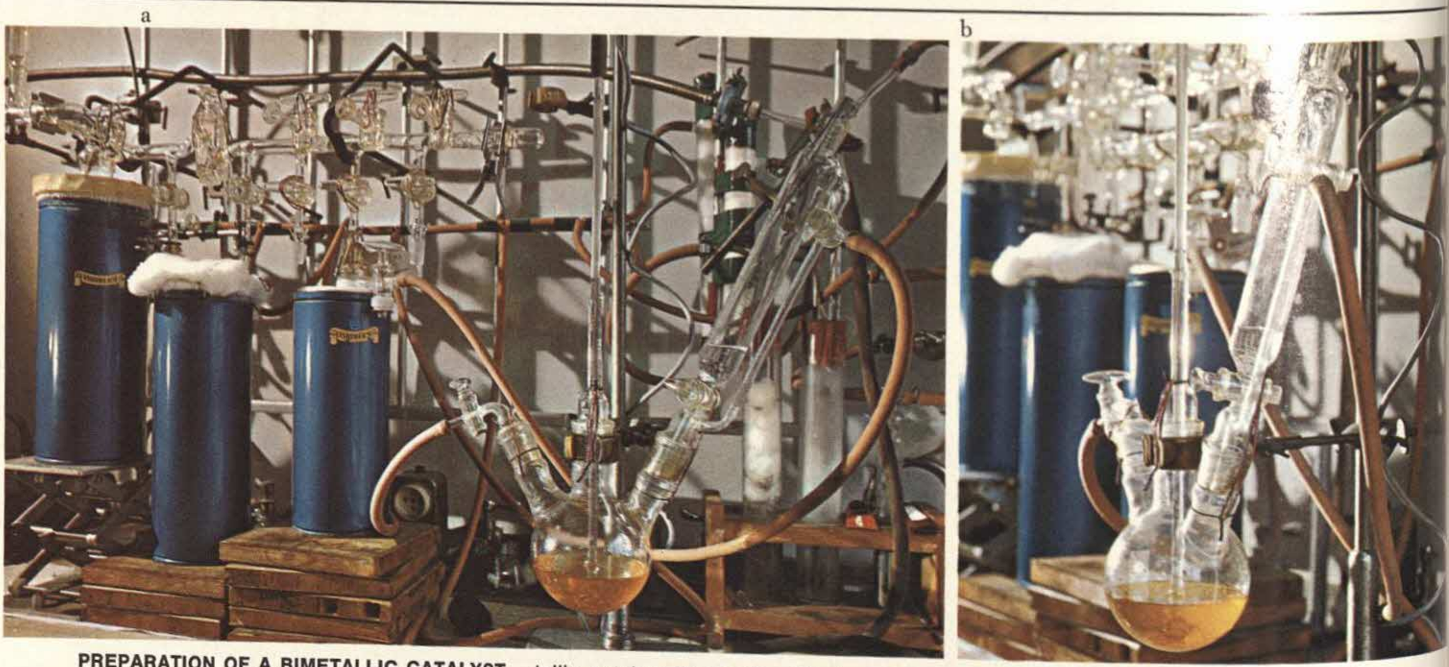
$C_2H_5^{\delta-}\text{—}MgBr^{\delta+} + {}^{\delta+}C(={}^{\delta-}O)(H)(H) \longrightarrow C_2H_5\text{—}C(H)(H)\text{—}BrMgO \xrightarrow[H_2O]{} C_2H_5CH_2OH$

formaldehyde

REACTION WITH OLEFINIC DOUBLE BONDS

$C_4H_9^{\delta-}\text{—}Li^{\delta+} + {}^{\delta+}CH_2={}^{\delta-}C(C_6H_5)(C_6H_5) \longrightarrow C_4H_9\text{—}CH_2\text{—}{}^-C(C_6H_5)(C_6H_5)\ Li^+$

diphenyl ethylene



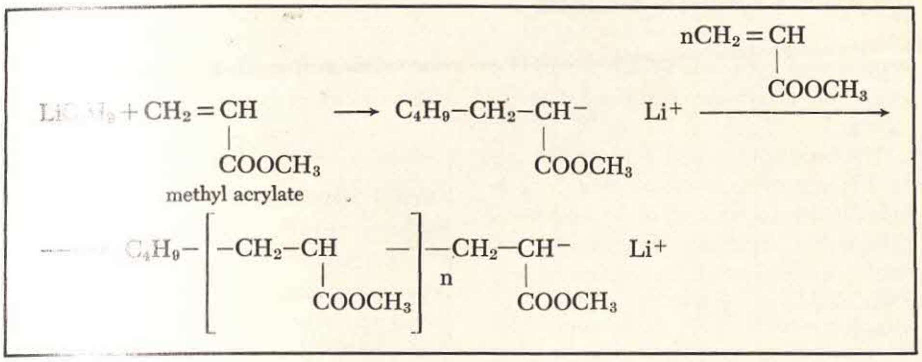
3

a

b

PREPARATION OF A BIMETALLIC CATALYST —The use of organometallic compounds always requires special precautions, primarily a dry, oxygen-free atmosphere. Illustrations 3a and 3b show the setup for preparing a bimetallic catalyst by reacting titanium tetrachloride ($TiCl_4$) with triethyl aluminum $Al(C_2H_5)_3$ in a nitrogen atmosphere. In the reaction, a chlorine atom changes place with an ethyl group to form $Ti(C_2H_5)Cl_3$ and $Al(C_2H_5)_2Cl$. The alkyltitanium chloride immediately loses the ethyl group to precipitate as $TiCl_3$ and this in combination with the diethyl aluminum chloride forms the catalyst.

in polymerizations based on an anionic mechanism:



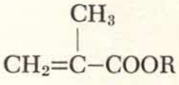
$$LiC_4H_9 + CH_2{=}\underset{\displaystyle COOCH_3}{CH} \longrightarrow C_4H_9{-}CH_2{-}\underset{\displaystyle COOCH_3}{CH^-}\quad Li^+ \xrightarrow{nCH_2=\underset{COOCH_3}{CH}} C_4H_9{-}\left[{-}CH_2{-}\underset{\displaystyle COOCH_3}{CH}{-}\right]_n{-}CH_2{-}\underset{\displaystyle COOCH_3}{CH^-}\quad Li^+$$

methyl acrylate

The most important organic compounds that undergo this type of reaction are:

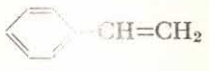
$CH_2{=}CH{-}COOR$

acrylic esters

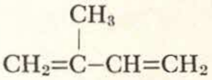


$$CH_2{=}\overset{\displaystyle CH_3}{C}{-}COOR$$

metacrylic esters



styrene



$$CH_2{=}\overset{\displaystyle CH_3}{C}{-}CH{=}CH_2$$

isoprene

In the early 1950s, a new series of catalysts were introduced by the German chemist Karl Ziegler and the Italian chemist Giulio Natta. These catalysts allowed the synthesis of numerous stereoregular polymers, among the most important of which is isotactic polypropylene. In recognition of their fundamental work, both scientists received the 1963 Nobel Prize in chemistry.

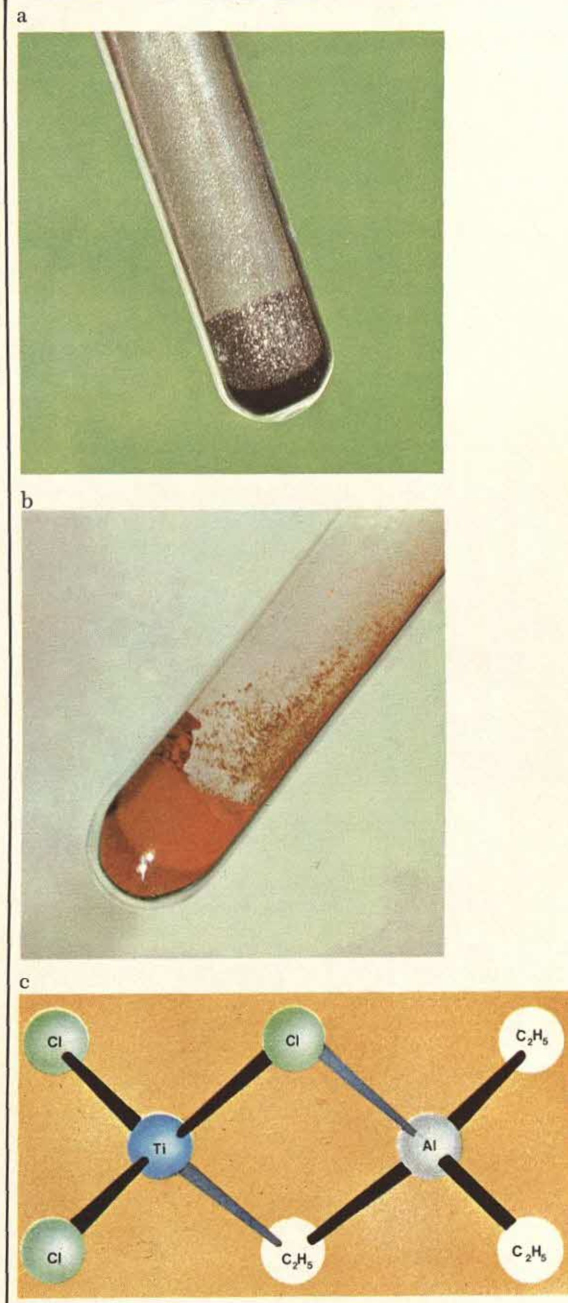
Ziegler's most important discovery was made in 1953. He and a student, E. Holzkamp, set out to repeat a preparation of higher aluminum alkyls by heating ethylene and aluminum triethyl; unexpectedly, they obtained a complete conversion of the ethylene monomer ($CH_2{=}CH_2$) to the dimer, butene-1 ($CH_3CH_2CH{=}CH_2$). The explanation was found in the presence of a trace of colloidal nickel derived from the catalyst used previously in an autoclave employed in hydrogenation experiments. This led to the discovery that substances made by mixing organometallic compounds with compounds of certain heavy metals permitted the fast polymerization of ethylene at atmospheric pressure to a linear polymer of high molecular weight having valuable plastic properties (other processes used high pressure and produced a partly branched polymer). The catalyst derived from aluminum alkyl and titanium tetrachloride proved especially useful and formed the basis of nearly all later developments in man-made plastics, fibers, rubbers, and films derived from such olefins as ethylene and butadiene.

Natta became best known for his discoveries after 1953, when he started intensive studies on macromolecular chemistry. These were initiated by knowledge of Ziegler's discovery of the low-pressure synthesis of linear polyethylene of high molecular weight. By applying the Ziegler catalysts to the polymerization of propylene, Natta found that part of the polymer was highly crystalline. He recognized that it must have been built up with a considerable degree of uniform three-dimensional, or steric, order, and proved the structure by the application of x-ray methods.

Natta then realized that the surface of the catalyst must also be highly regular to give rise to the isotactic polymer and then discovered variants of the Ziegler catalyst system that made possible the high-yield isotactic polymerization of propylene and other olefins.

Ziegler's and Natta's catalysts are produced by reacting organometallic compounds of metals from Groups I-III (aluminum, beryllium, zinc, and so forth) with derivatives of the transition metals of Groups IV-VIII (vanadium, titanium, cobalt, zirconium, and so forth). A typical example is provided by the complex compound triethyl aluminum-titanium trichloride, discovered by Natta. Thanks to polymerization processes, many organometallic compounds, particularly the aluminum alkyls, are now of considerable industrial importance.

4



THE NATTA CATALYSTS—Illustration 4a shows a small amount of a catalyst used in the low-pressure polymerization of olefins. This is the α-form (violet) composed of $TiCl_3$ and triethyl aluminum. The β-form of the compound is seen as an orange-red powder in Illustration 4b.

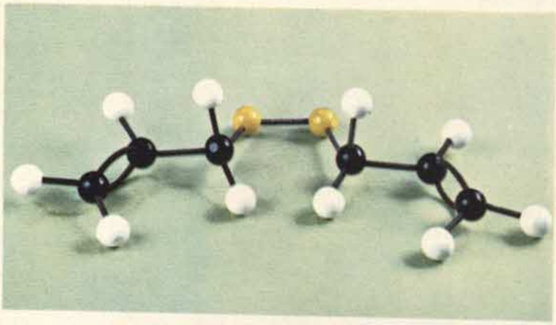
The structural diagram in Illustration 4c represents the complex compound formed by the reagents in the catalyst. The typical bridge structure that forms the active center of the polymerization results from secondary bonds.

ORGANIC DERIVATIVES OF SULFUR

mercaptans, sulfides, and their oxidation products

Paralleling the oxygen-containing organic compounds, the organic derivatives of sulfur comprise a large group of substances with varying degrees of industrial importance. Preparation of these materials is relatively straightforward, though the processes and the products often make themselves known by an overwhelming stench. In fact, some organic sulfur compounds can be smelled for miles from their source, even when in minuscule concentrations.

1



ALLYL DISULFIDE—This compound, with the formula $CH_2{=}CH-CH_2-S-S-CH_2-CH{=}CH_2$, is a liquid with a boiling point of 139° C (282.2° F). Its pungent odor is immediately recognized in garlic. In fact, the Latin for garlic, *Allium sativum*, provides the name for the allyl radical ($-CH-CH{=}CH_2$). All the derivatives containing this radical are known as allyl compounds.

When the oxygen atoms in organic compounds are replaced by atoms of sulfur, the result is a series of compounds of which the more important are mercaptans, sulfides, and disulfides. The materials are formed in exchange reactions with alcohols, ethers, and peroxides, respectively:

$$\underset{\text{alcohols}}{R-OH}$$

$$\underset{\text{ethers}}{R-O-R'}$$

$$\underset{\text{peroxides}}{R-O-O-R'}$$

$$\underset{\text{mercaptans}}{R-SH}$$

$$\underset{\text{sulfides}}{R-S-R'}$$

$$\underset{\text{disulfides}}{R-S-S-R'}$$

In these general formulas, the groups represented by R and R′ are the alkyl or aryl type, and may be the same or dissimilar.

The mercaptans and sulfides can also be thought of as monosubstituted or bisubstituted derivatives of hydrogen sulfide, H_2S. Chemically, they exhibit similarities to the alcohols and ethers, although their reactivity generally is more pronounced.

Other types of sulfur-containing organic compounds can be derived from the mercaptans and sulfides. Such derivatives correspond to sulfur at higher degrees of oxidation. Thus:

$$\underset{\text{mercaptan}}{R-SH} \rightarrow \underset{\text{sulfinic acid}}{R-SO-OH} \rightarrow \underset{\text{sulfonic acid}}{R-SO_2-OH}$$

$$\underset{\text{sulfide}}{R-S-R'} \rightarrow \underset{\text{sulfone}}{R-SO-R'} \rightarrow \underset{\text{sulfoxide}}{R-SO_2-R'}$$

MERCAPTANS OR THIOALCOHOLS

One characteristic of the mercaptans that serves to distinguish them from alcohols is the ease with which they react with mercury oxide:

$$2\underset{\substack{\text{ethyl}\\\text{mercaptan}}}{C_2H_5SH} + HgO \rightarrow \underset{\substack{\text{mercuric ethyl}\\\text{mercaptide}}}{(C_2H_5S)_2Hg} + H_2O.$$

The same ease of reaction is observed with the salts of heavy metals in solution. In both types of reaction, the products are crystalline compounds called mercaptides.

The mercaptides correspond to the alcoholates, as seen in

$$\underset{\substack{\text{sodium methyl}\\\text{mercaptide}}}{CH_3SNa}$$

$$\underset{\text{sodium methylate}}{CH_3ONa}$$

but are more easily formed and are more stable. The stability of the mercaptides results from the hydrogen-sulfur bond and a resultant acidic character.

The mercaptans have lower boiling points than the alcohols because of hydrogen's diminished tendency to form bonds and a concurrent lower degree of association. This can be likened to hydrogen sulfide, whose boiling point is considerably lower than that of water—so low, in fact, that H_2S is a gas at room temperature.

sulfur derivatives	boiling point
H_2S	−60.7° C
CH_3SH	+ 6
C_2H_5SH	+37
oxygen derivatives	**boiling point**
H_2O	+100° C
CH_3OH	+ 64.9
C_2H_5OH	+ 78.5

Mercaptans are colorless liquids, either insoluble or only slightly soluble in water. Their most apparent characteristic is an unpleasant, penetrating odor, which makes them easily recognizable even in minimal concentrations.

Aliphatic mercaptans are prepared in the laboratory using several procedures, including the following:

1. The reaction between an alkylating agent (alkyl sulfates or halides) and potassium hydrosulfide.

$$\underset{\substack{\text{dimethyl}\\\text{sulfate}}}{(CH_3)_2SO_4} + 2KSH \rightarrow 2\underset{\substack{\text{methyl}\\\text{mercaptan}}}{CH_3SH} + K_2SO_4$$

This simple exchange reaction is performed with the addition of heat, and the mercaptan vapors are easily condensed and collected.

2. The substitution of oxygen in alcohols with phosphorus pentasulfide.

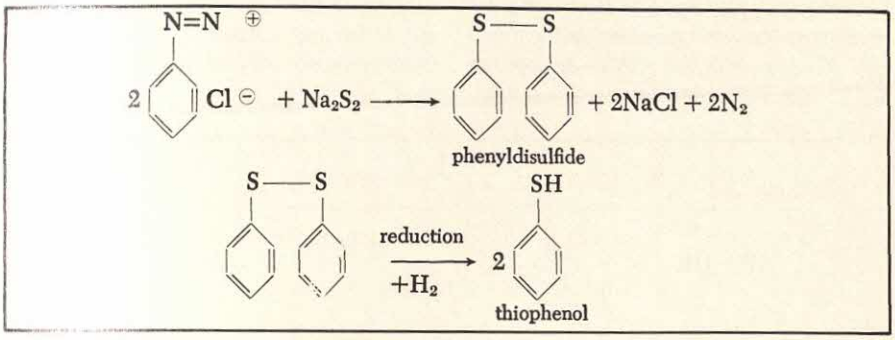
$$5C_2H_5OH + P_2S_5 \rightarrow 5C_2H_5SH + P_2O_5.$$

In both these reactions, the yields are relatively small. Thus, on an industrial scale the mercaptans are produced by reacting an alcohol with hydrogen sulfide in the presence of a thorium oxide catalyst at temperatures from 300 to 350° C (from 572 to 662° F):

$$R-OH + H_2S \rightarrow R-SH + H_2O.$$

One of the more important aliphatic mercaptans is ethyl mercaptan (C_2H_5SH). This is used as an intermediate in the preparation of certain hypnotics. Ethyl mercaptan is a product of the first type of reaction.

Of the aromatic mercaptans, the most important is thiophenol, a colorless, foul-smelling liquid with a boiling point of 169° C (336.2° F). In the laboratory, this compound can be prepared by reacting phenyldiazonium chloride and sodium disulfide with subsequent reduction of the phenyldisulfide product:



The aromatic mercaptans display a marked acidity and form stable salts with metals.

Some of the more characteristic reactions of the aliphatic and aromatic mercaptans are:

1. Vigorous oxidation, with nitric acid for example, leading to the formation of sulfonic acids.

$$R{-}SH + 3O \rightarrow R{-}SO_2{-}OH$$

2. Moderate oxidation by weak oxidizing agents (iodine, for example) to convert mercaptans into disulfides.

$$2R{-}SH + O \rightarrow R{-}S{-}S{-}R + H_2O$$

A reaction of this type is used in the oil-refining industry where mercaptans are oxidized with an alkaline solution of sodium plumbite in an operation known as "sweetening."

The disulfides are liquids with an intense, nauseating odor. These compounds are insoluble in water and are easily reduced to mercaptans in reactions such as

$$\underset{\text{methyl disulfide}}{CH_3{-}S{-}S{-}CH_3} + 2Na_2S$$

$$\rightarrow \underset{\substack{\text{sodium methyl}\\ \text{mercaptide}}}{2CH_3SNa} + Na_2S_2.$$

The characteristic −S−S− group of the disulfides is also found in the very complex molecules of sulfur dyes.

SULFONIC ACIDS

Through oxidation reactions, two classes of compounds are obtained from the mercaptans. They are the sulfinic acids, in which the −SO−OH group is bound to a carbon atom, and the sulfonic acids, which contain an $-SO_2{-}OH$ group bonded to a carbon atom. Of the two classes, the sulfonic acids have the greater interest and importance.

Exhibiting an acidity comparable to that of the mineral acids, sulfonic acids form stable and generally well-crystallized salts with the metals. In appearance, these acids are syrupy liquids or crystalline solids; in either case they are highly soluble in water.

The distinction between alkylsulfonic and arylsulfonic acids must be emphasized, not only because of differences in method of preparation, but also because of important dissimilarities in their reactivity characteristics.

The methods for synthesizing alkylsulfonic acids include mercaptan oxidation and the alkylation of inorganic sulfites, as seen in these reactions:

$$\underset{\substack{\text{methyl}\\ \text{mercaptan}}}{CH_3SH} \xrightarrow{O} \underset{\substack{\text{methanesulfonic}\\ \text{acid}}}{CH_3{-}SO_2{-}OH}$$

$$\underset{\substack{\text{methyl}\\ \text{iodide}}}{CH_3I} + \underset{\substack{\text{potassium}\\ \text{sulfite}}}{K_2SO_3} \longrightarrow \underset{\substack{\text{potassium salt of}\\ \text{methanesulfonic acid}}}{CH_3{-}SO_2{-}OK} + KI$$

While these reactions are particularly suited to small-scale laboratory production, they are not economically applicable on an industrial scale. Major production is carried out by the direct sulfonation of paraffins with a mixture of sulfur dioxide and chlorine in the presence of heat. Sulfuric acid can be used in this reaction in place of the sulfur dioxide, although the results are far from satisfying.

Alkylsulfonic acids are very stable compounds that are acted on by phosphorus pentachloride to yield the corresponding chlorides having the general formula $R{-}SO_2{-}Cl$. These chlorides are reducible to sulfinic acids and mercaptans:

$$R{-}SO_2{-}Cl \underset{-HCl}{\xrightarrow{+H_2}} \underset{\substack{\text{sulfinic}\\ \text{acid}}}{R{-}SO{-}OH} \underset{-H_2O}{\xrightarrow{+H_2}} R{-}SH$$

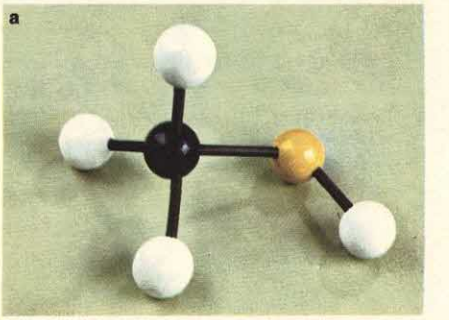
One derivative of this class has found practical application in x-ray therapy because of its opacity to this radiation. This

2

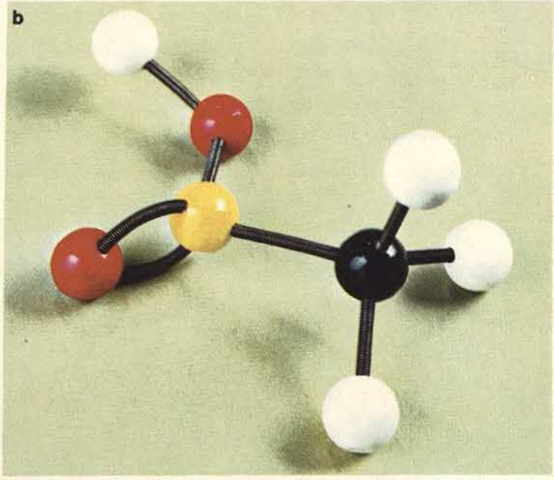
FROM MERCAPTAN TO SULFONIC ACID— The models depicted here show the sequence in the conversion of methyl mercaptan (Illustration 2a) to methanesulfinic acid (Illustration 2b) and finally to methanesulfonic acid (Illustration 2c). This is an oxidation reaction made possible by the unstable nature of sulfinic acids.

Methanesulfonic acid, obtained industrially as a by-product in oil refining, is used as a catalyst in many organic reactions, including hydrolysis, alkylation, and esterification.

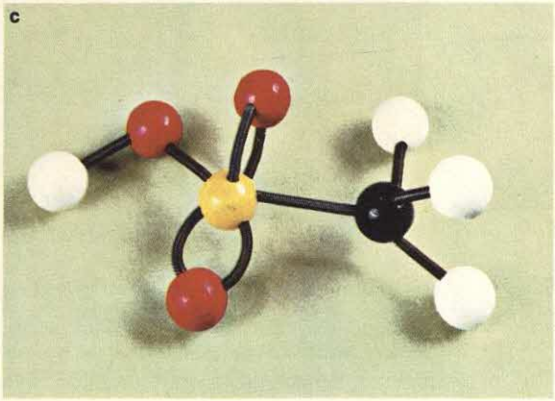
a



b



c



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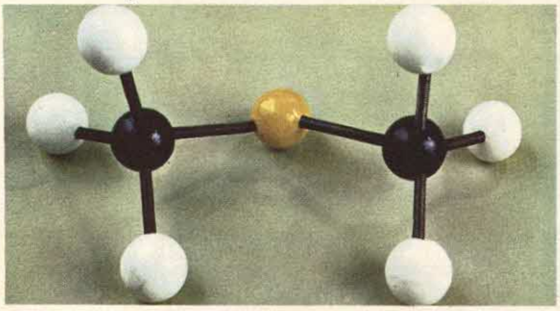
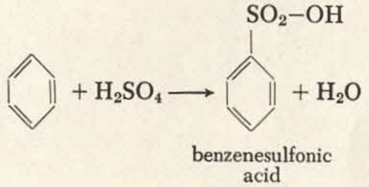


METHYL SULFIDE—First synthesized by the German chemist Friedrich August Kekulé, the organic sulfides are somewhat analogous to the ethers, differing by the presence of a sulfur atom in place of an oxygen atom. These compounds are known as thioethers. This illustration shows a model of methyl sulfide, CH_3-S-CH_3, a liquid with a penetrating odor.

compound is the sodium salt of iodomethanesulfonic acid (ICH_2-SO_2-ONa).

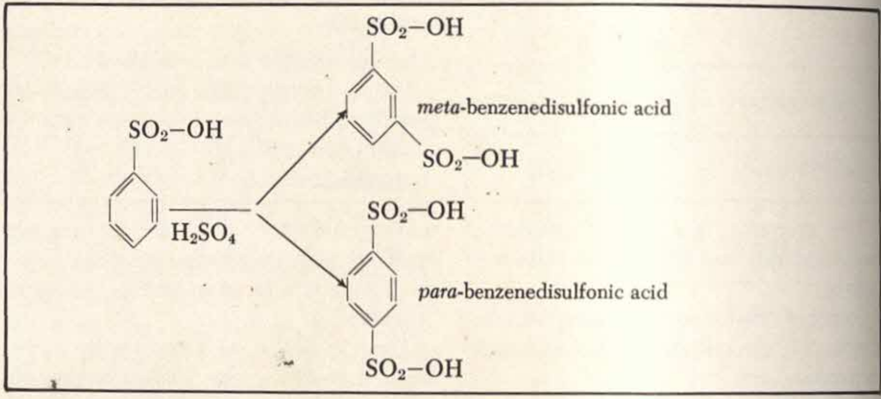
The arylsulfonic acids, unlike their aliphatic homologues, are readily obtained by the action of sulfuric acid on the aromatic hydrocarbons. The simplicity of this reaction gives it considerable technologic importance.



benzenesulfonic acid

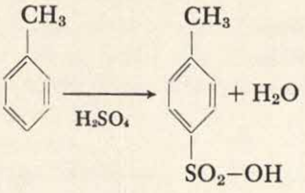
Sulfuric acid loses its effectiveness as a sulfonating agent when its concentration falls below 65 percent; therefore, the reaction is performed at temperatures from 170 to 180° C (from 338 to 356° F). This serves to eliminate the water formed, thus maintaining the concentration at a usable level. The arylsulfonic acid product is separated from the excess sulfuric acid by saturating the final mixture with sodium chloride, an operation called "salting." The precipitated sodium arylsulfonate is then recovered.

Sulfonation of the aromatic nucleus can be forced to the extent that two or three sulfonic groups are accepted. In order to accomplish this, however, the reaction must be carried out with the aid of fuming sulfuric acid (H_2SO_4 containing excess SO_3, sulfur trioxide) and heat.



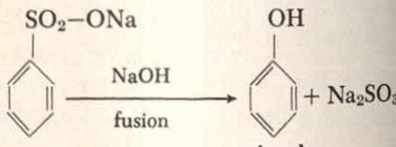
A third acid, *ortho*-benzenedisulfonic acid, can be formed in this reaction, but its quantity is insufficient to make its extraction worthwhile.

If toluene is sulfonated, the principal product is the *para*-acid:

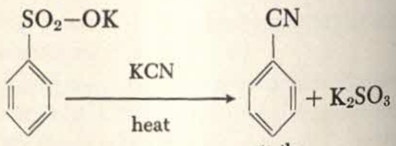


para-toluenesulfonic acid

The importance of the arylsulfonic acids derives from the ease and low cost of production and from the reactivity of the sulfonic group bound to the aromatic nucleus. The following are examples of applications of the arylsulfonic acids as intermediates in organic synthesis.

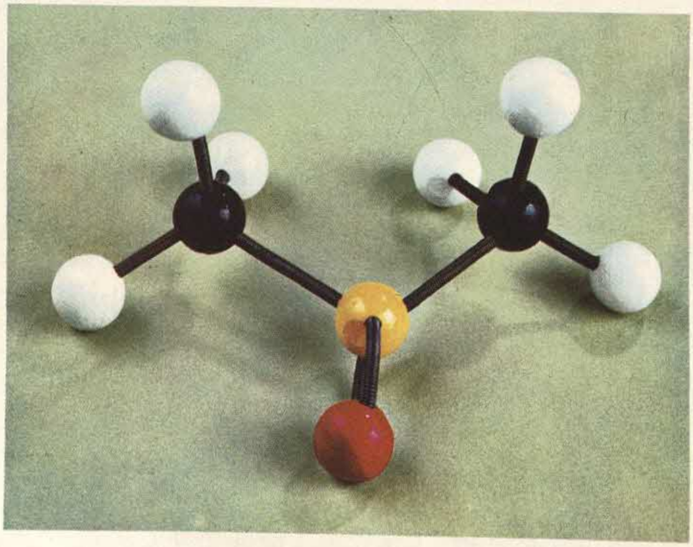


phenol

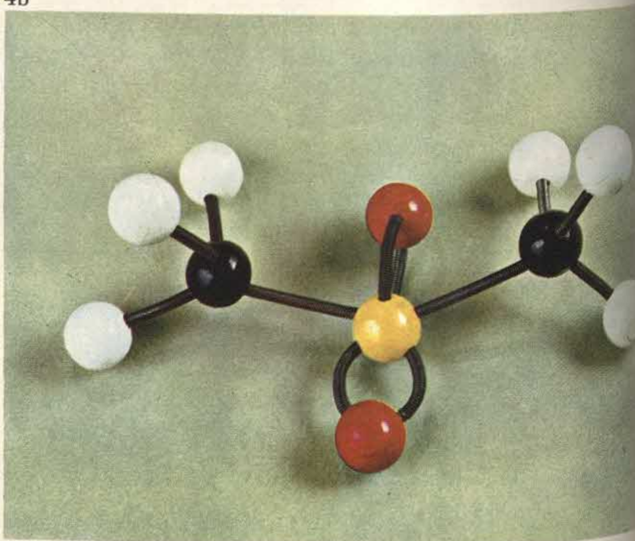


nitrile

4a



4b



DIMETHYL SULFOXIDE AND METHYL SULFONE—Dimethyl sulfoxide (Illustration 4a) is a product of the reaction between methyl sulfide and hydrogen peroxide. It is a compound that melts at 6° C (42.8° F) and decomposes at 100° C (212° F) and is a powerful solvent for many organic and even inorganic compounds. Further oxidation produces methyl sulfone (Illustration 4b), a solid material with a melting point of 109° C (228.2° F).

The sulfones are important in medicine, providing a source of valuable derivatives. One derivative, with the formidable name 4,4'-diaminodiphenylsulfone (DDS for short), has made possible the eradication of leprosy.

In a similar manner, the chlorides of arylsulfonic acids, RSO_2Cl, can be reduced to sulfinic acids and thiophenols.

SULFIDES OR THIOETHERS

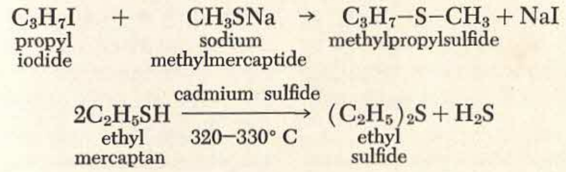
Organic sulfides with low molecular weights are colorless liquids, insoluble in water but soluble in alcohols and ethers. When pure, these compounds have pleasant odors.

The thioethers have boiling points higher than the corresponding mercaptans in contrast with the oxygen-containing ethers, which are more volatile than their corresponding alcohols.

mercaptans	boiling point	sulfides	boiling point
CH_3SH	+ 6° C	$(CH_3)_2S$	+38° C
C_2H_5SH	+37	$(C_2H_5)_2S$	+91

The increased boiling points are explained by a low degree of association in the organic sulfur derivatives. In a comparison of them and oxygen derivatives, the elevated boiling points are displayed by the compounds with greater molecular weights, the thioethers.

The following production methods for thioethers show an analogy to the processes used in ether syntheses:



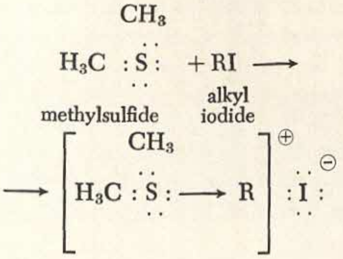
$$\underset{\text{propyl iodide}}{C_3H_7I} + \underset{\text{sodium methylmercaptide}}{CH_3SNa} \rightarrow \underset{\text{methylpropylsulfide}}{C_3H_7{-}S{-}CH_3} + NaI$$

$$\underset{\text{ethyl mercaptan}}{2C_2H_5SH} \xrightarrow[320-330°\ C]{\text{cadmium sulfide}} \underset{\text{ethyl sulfide}}{(C_2H_5)_2S} + H_2S$$

Another method of synthesis exists, however, for which there is no equivalent in the chemistry of organic oxygen derivatives. This method involves the heating of lead or mercury mercaptides:

$$(C_2H_5S)_2Pb \rightarrow (C_2H_5)_2S + PbS.$$

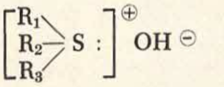
Organic sulfides give rise to many interesting reactions, among which are the oxidation reactions leading to the formation of sulfoxides and sulfones. A fundamental characteristic of the sulfides is their ability to add halogens, metal salts, and alkyl halogenides. The resulting compounds in such reactions are called sulfonium salts; they are analogous to oxonium and ammonium salts obtained from ethers and amines, respectively. In fact, like oxygen and nitrogen, sulfur is strongly basic because it tends to give up two free electrons in bond formation.



$$\underset{\text{methylsulfide}}{H_3C : \overset{CH_3}{\ddot{S}} :} + \underset{\text{alkyl iodide}}{RI} \longrightarrow \left[H_3C : \overset{CH_3}{\ddot{S}} : \longrightarrow R \right]^{\oplus} : \ddot{I} :^{\ominus}$$

In the mechanism of this reaction, the R group attracts and keeps a positive charge, thereby leaving the iodine with a negative charge. The pair of bond electrons is supplied by the sulfur. Like metallic salts, the resulting compound tends to form ions on dissociation in an aqueous solution.

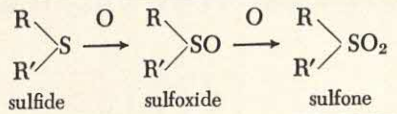
The three radicals and residual pairs of electrons in sulfonium salts are distributed around the central sulfur atom, at the vertices of a tetrahedron. By means of a double exchange reaction with silver hydroxide, the sulfonium salts become



sulfonium hydroxides, and these are characterized by a basicity comparable to that of the alkaline hydroxides.

SULFOXIDES AND SULFONES

Sulfoxides are obtained from the sulfides through oxidation with hydrogen peroxide or dilute nitric acid at room temperature. At higher temperatures, or with stronger oxidizing agents, the reaction leads to sulfone production, as shown in these equations:



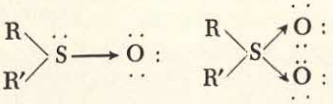
For example, ethyl sulfoxide, $(C_2H_5)_2SO$, a liquid that freezes at 4 to 6° C (39.2 to 42.8° F), is synthesized by oxidizing ethyl sulfide with hydrogen peroxide in acetic acid while the reaction is cooled. If the temperature of the reaction is allowed to rise, the product is ethyl sulfone, $(C_2H_5)_2SO_2$, a crystalline solid that fuses at 73° C (163.4° F).

The sulfoxides have a tendency to form compounds by addition, because the sulfur atom still has an available electron pair. Thus, the compounds of methyl and ethyl sulfoxide can be obtained with nitric acid,

$$(C_2H_5)_2SO \cdot HNO_3,$$

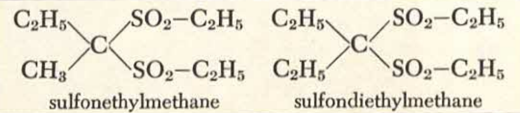
from which the sulfoxide can be recovered by treating the compound with barium carbonate. Unlike the sulfones, the sulfoxides can be reduced to sulfides by nascent hydrogen.

In the sulfoxides and sulfones, the S–O bonds are the semipolar variety, meaning that the pair of bond electrons is not formed by two electrons, one donated from the sulfur and one from the oxygen. Rather, the electron pair is supplied exclusively by the sulfur:



The arrangement of the four atoms or groups around the central sulfur atom in the sulfones is tetrahedral.

The sulfone group includes a number of compounds with a marked narcotic action: sulfonmethane, sulfonethylmethane, sulfondiethylmethane. Significantly, the narcotic activity increases as more and more ethyl groups are added to replace methyl groups, as in sulfonethylmethane and sulfondiethylmethane:



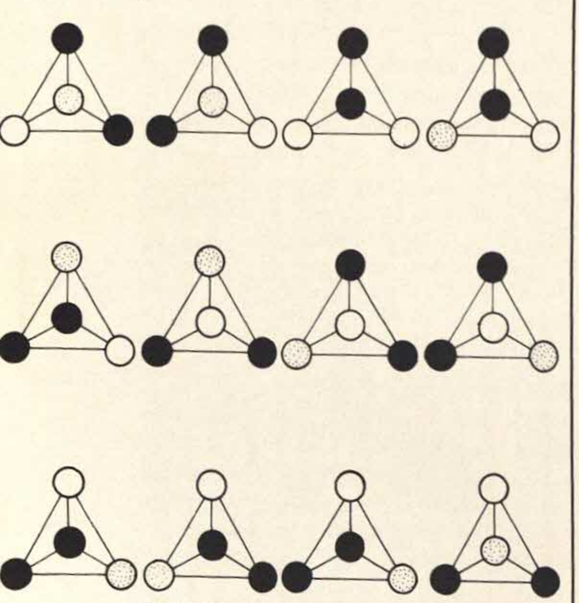
Sulfone group compounds were introduced into therapeutics between 1884 and 1888. Sulfonmethane (Sulfonal) is slowly absorbed from the intestinal tract; depression after awakening may be severe. Because the drug is slowly excreted, toxic cumulation may occur during continuous administration. Death from overdosage results from respiratory and circulatory failure. Chronic poisoning causes mental and gastrointestinal symptoms and urinary changes. Other toxic manifestations may appear in the skin, liver, and kidneys. Sulfonethylmethane is absorbed more rapidly than Sulfonal, sulfondiethylmethane more slowly.

OPTICAL ISOMERISM | mirror images of molecules

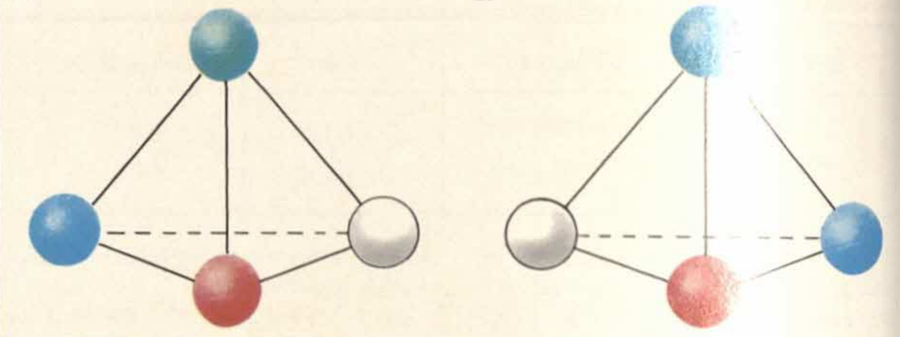
Of the two types of stereoisomerism, geometric and optical, the latter is encountered frequently in naturally occurring organic molecules and processes. Not the least of these are the functions seen in human physiology. As might be expected, optical isomerism deals with the manner in which different atomic arrangements of the same compound affect the rotation of light—specifically, the plane of polarization of polarized light. The subject of optical isomerism is not so forbidding as it may appear, especially if the first step is an examination of the simplest hydrocarbon molecule, methane.

The single carbon atom in methane dictates that the molecule will take on a tetrahedral shape. Furthermore, this configuration is characteristic when all four of carbon's bonds are saturated. If any one of the hydrogen atoms in methane is replaced by some other atom or group, the new compound thus formed will be the same no matter which hydrogen atom is replaced. The identical thing occurs even when two of the four hydrogen atoms are replaced by two different atoms or groups. This compound will be the same, unto itself, without regard to which hydrogen atoms have been substituted.

1



DISUBSTITUTED METHANE—If two hydrogen atoms in the methane molecule are replaced by different groups, no matter what their position the new molecules will be identical. (In these structures, the central carbon atom is not shown.)



2a

2b

ENANTIOMERS — If three of the hydrogen atoms in a methane molecule are substituted, the result is two molecules that are mirror images of one another (Illustrations 2a and 2b). Such molecules are not identical.

A study of Illustration 1 points out that irrespective of the positions occupied by the substitutes, the molecules can always be made to coincide by rotation and are, therefore, identical. However, when more than two of methane's hydrogen atoms are replaced by different atoms or groups, an entirely new story develops.

In general terms, when an organic molecule is structured so that four dissimilar atoms or groups are bound to a tetrahedral carbon atom, the molecule can exist in two different forms. Furthermore, these forms will be mirror images of one another. Isomers of this type are called enantiomorphs or enantiomers from the Greek *enantios,* meaning "opposite."

Although the physical properties of enantiomorphic compounds are identical (except for the direction in which they rotate plane-polarized light), they are chemically different. However, in most reactions between optical isomers or reactions occurring in living organisms, enantiomorphs of the same compound act like chemically different substances, and therefore, they must for practical purposes be regarded as such.

With respect to their physical properties, enantiomers are seen to be identical in ordinary characteristics (melting and boiling points, for example), but are quite individual when it comes to special properties such as x-ray diffraction and rotation of polarized light. In the latter regard, two forms of an optical isomer cause the plane of polarized light to rotate through the same angle in terms of absolute value. However, one will cause clockwise rotation while the other rotates the plane in a counterclockwise fashion. In the first instance, the isomer is said to be dextrorotary and is indicated by a plus sign (+); the second isomer is called levorotary and is designated by a minus sign (−).

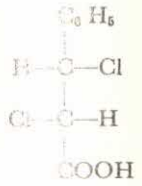
This type of stereoisomerism is called optical isomerism, and the two forms of the enantiomorph are said to be optical antipodes, or opposites. A mixture consisting of equal parts of the optical antipodes makes up a form of the compound called racemic, referring to the fact that it will not cause any rotation in a plane of polarized light. This is understandable because the rotative contributions of the two enantiomers are equal in value, but of opposite sign, and thus cancel each other's effect.

In working with racemic compounds, the problem of their separation into the two optically active forms (optical antipodes) often arises, notably in organic synthesis. The identical physical characteristics of the enantiomers are not shared by the racemic form, effectively eliminating separation by mechanical means or by crystallization. In some cases, a microbiological separation may be effected by using an organism able to destroy one form, leaving the other intact.

This method is limited, however, because it necessarily renders one of the antipodes useless for study.

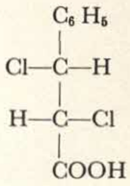
The chemical methods, therefore, are far more practical and important. To understand them, however, a few new concepts concerning optical isomerism must be added.

The compounds so far discussed have contained only one asymmetric carbon atom; that is, a carbon with four different substituents. Matters become considerably more complex as molecules with several asymmetric (or dissymmetric) carbons are studied. Steps toward clarification can begin with an examination of a compound with two asymmetric carbon atoms:



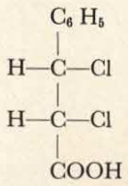
$$\begin{array}{c} C_6H_5 \\ | \\ H-C-Cl \\ | \\ Cl-C-H \\ | \\ COOH \end{array}$$

(a)



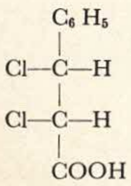
$$\begin{array}{c} C_6H_5 \\ | \\ Cl-C-H \\ | \\ H-C-Cl \\ | \\ COOH \end{array}$$

(b)



$$\begin{array}{c} C_6H_5 \\ | \\ H-C-Cl \\ | \\ H-C-Cl \\ | \\ COOH \end{array}$$

(c)



$$\begin{array}{c} C_6H_5 \\ | \\ Cl-C-H \\ | \\ Cl-C-H \\ | \\ COOH \end{array}$$

(d)

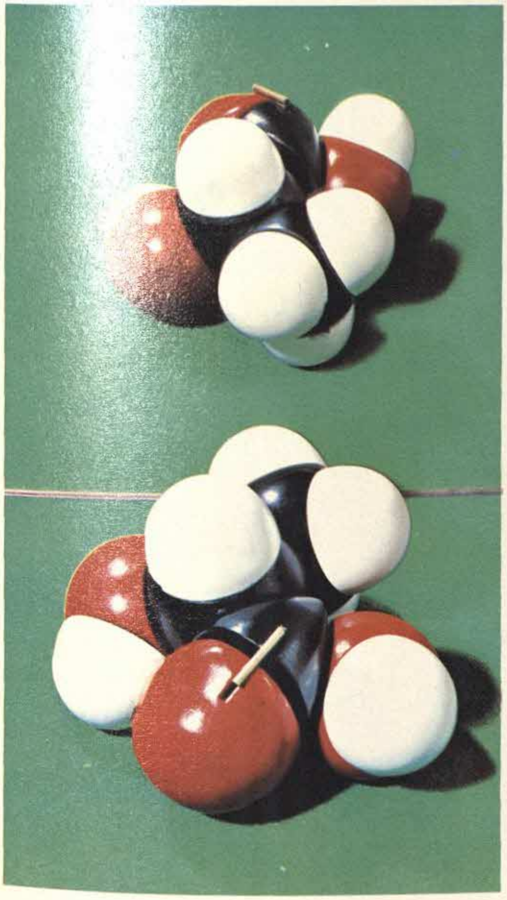
Immediately apparent is that an increase in the number of asymmetric carbon atoms leads to an increase in the number of isomers. Further study will show that there are two pairs of enantiomers; (a) and (b) are one, and (c) and (d) the other; and that in each pair the individual molecules are mirror images. Also, (a,c) and (b,d) constitute pairs of different forms, as do (a,d) and (b,c). These forms that are not mirror images are called diastereomers, and they have disparate properties that allow easy separation.

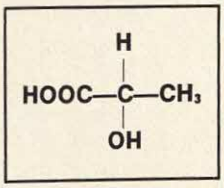
The decomposition of a racemic form is, therefore, accomplished by the synthesis of two diastereomers. For example, if the racemic form is an acid, it can be reacted with an optically active base to produce two diastereomeric salts. When, in turn, these are separated, it is

LACTIC ACID—Bound to the central carbon atom in lactic acid are four different groups: —H, —OH, —COOH, and —CH_3. The configurations in both illustrations represent optically active forms of the acid. In fact, one of the forms was placed in front of a mirror to obtain each illustration.

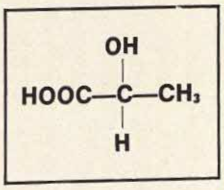
The molecule represented in Illustration 3a is probably closest to reality with regard to the scale of atomic dimension and interatomic distances. However, the same molecule as shown in Illustration 3b is more typical of optical isomerism. In both, the white spheres indicate hydrogen, the red oxygen, and the black carbon.

3a



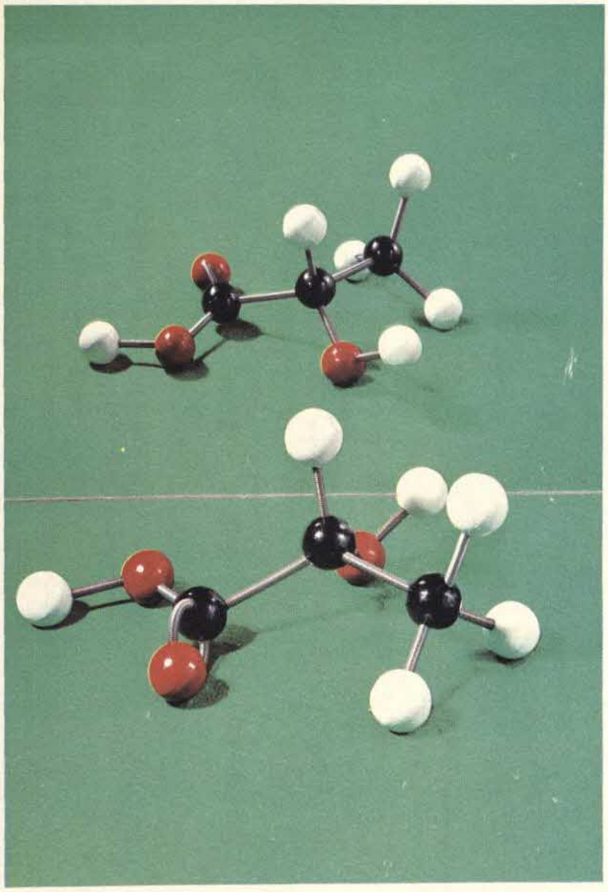


$$\begin{array}{c} H \\ | \\ HOOC-C-CH_3 \\ | \\ OH \end{array}$$



$$\begin{array}{c} OH \\ | \\ HOOC-C-CH_3 \\ | \\ H \end{array}$$

3b



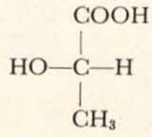
possible to obtain two optically active acids.

$$\text{racemic form} \begin{cases}\text{acid } (+)\\ \text{acid } (-)\end{cases}$$

$$+ \text{ base } (+) \rightarrow 2 \text{ diastereomeric forms of the salt}$$

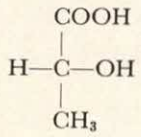
LACTIC ACID

An interesting example of optical activity in a compound is provided by lactic acid. In α-lactic acid, the central carbon atom is bound to four different groups and is, therefore, asymmetric.



$$\begin{array}{c}\text{COOH}\\ |\\ \text{HO—C—H}\\ |\\ \text{CH}_3\end{array}$$

lactic acid (+)



$$\begin{array}{c}\text{COOH}\\ |\\ \text{H—C—OH}\\ |\\ \text{CH}_3\end{array}$$

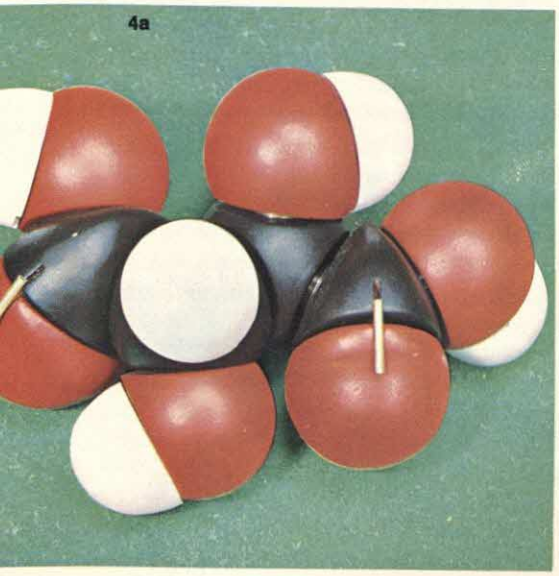
lactic acid (−)

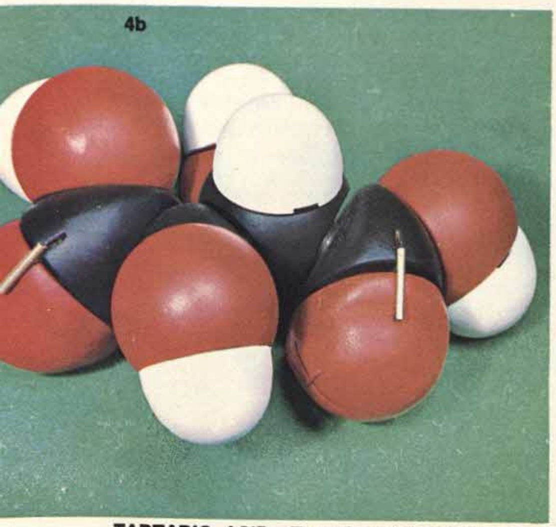
The isomers of this essential organic acid can exist in any of three forms:

1. Dextrorotary lactic acid, with a melting point of 26° C (78.8° F), is found in muscle tissue where it is formed during periods of physical exertion. In the laboratory it can be obtained by the oxidation of α-D-6-deoxyaminopyranoside. Dextrorotary lactic acid is optically active.

2. The levorotary form, also with a melting point of 26° C, is familiar to anyone who has ever tasted sour milk, in which it is produced during fermentation. An interesting sidelight is that certain fermentation bacteria are also capable of producing the dextrorotary and racemic forms of the acid. Synthetically, lactic acid (−) is made by oxidizing α-L-5-deoxyarabinofuranoside. The levorotary form is optically active.

3. Racemic lactic acid (±) is the iso-

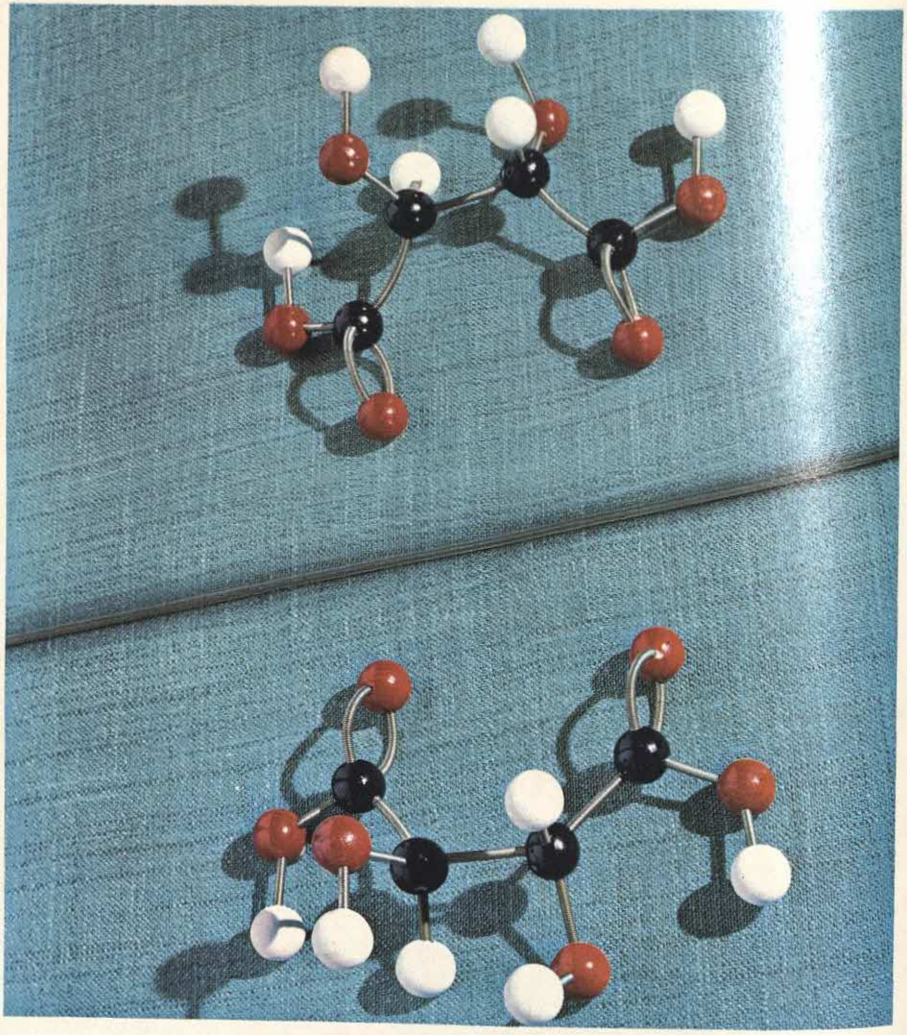




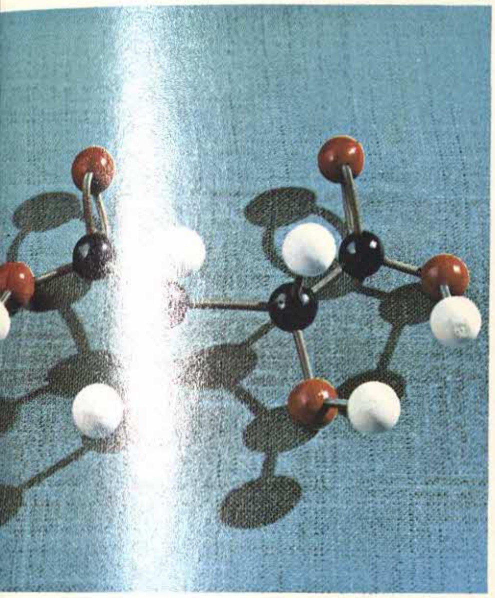
TARTARIC ACID—Tartaric acid contains two equivalent asymmetric carbon atoms, meaning that each is bound to identical atoms or groups. Illustrations 4a and 4b are the mirror image forms of this compound.

EXPANDED MOLECULAR MODELS OF TARTARIC ACID—These molecules are identical to those in the previous illustration, but with an expansion of the bonds between the atoms comes a clearer understanding of these optical antipodes.

5



6



THE MESO-FORM OF TARTARIC ACID—In addition to the dextrorotary and levorotary forms of tartaric acid, this compound also exists as the optically inactive *meso*-form. The molecule in this state is symmetric about a plane that divides it equally into two asymmetric parts.

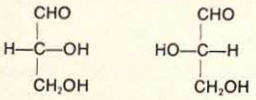
mer produced in the course of normal laboratory synthesis. Unlike the other two forms, this has a melting point of 18° C (64.4° F). Racemic lactic acid is optically inactive.

TARTARIC ACID

A classic example of a compound with more than one asymmetric carbon atom is provided by tartaric acid, the acid in grapes. This acid contains two equivalent asymmetric carbon atoms so that the substituents bound to one are equal to those bound to the other. Thus, each carbon atom is bound to one −H, one −OH group, a −COOH group, and to one HO$-\overset{|}{\mathrm{C}}$H$-$COOH chain. All compounds of this type present not only the usual forms, but also the so-called optically inactive *meso*-form.

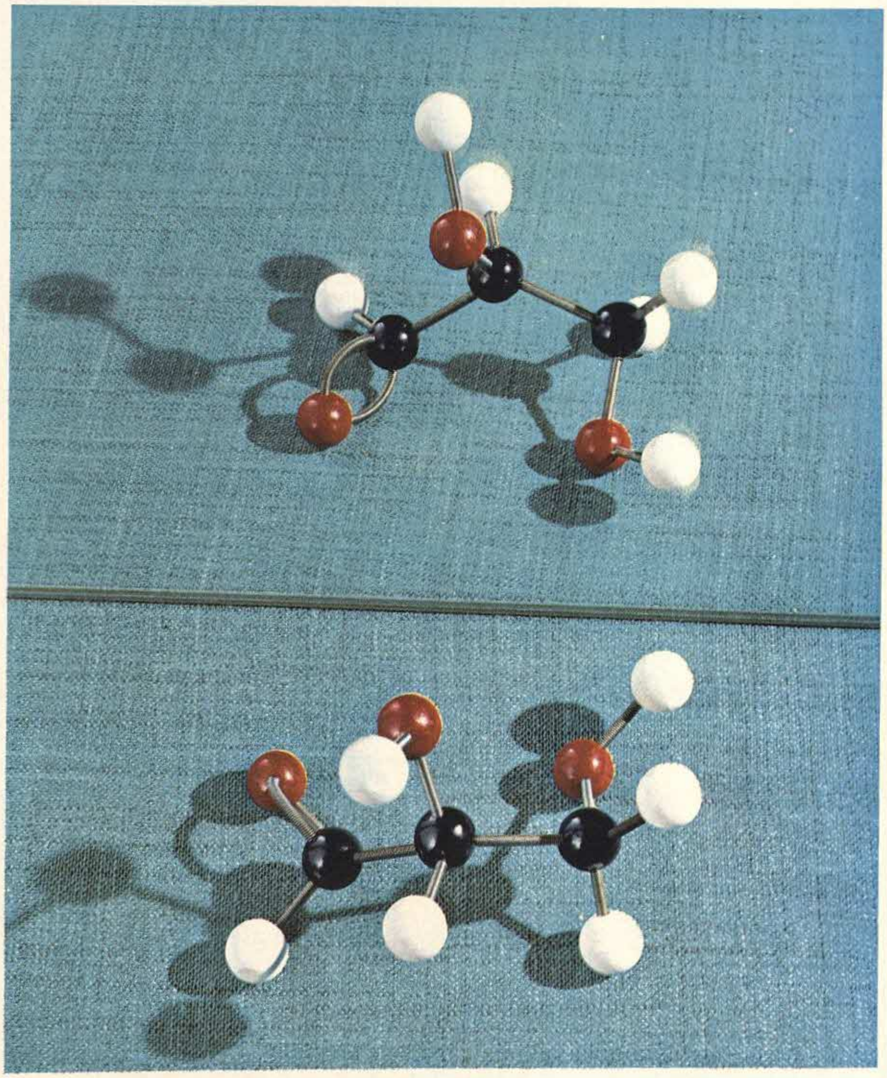
In the latter, if the molecule is equally divided, each half shows asymmetry while as a whole the molecule is decidedly symmetrical. The physical properties of the *meso*-form are noticeably different from those of the racemic form and the two optical antipodes. The illustration to the right shows some of the details of tartaric acid's forms.

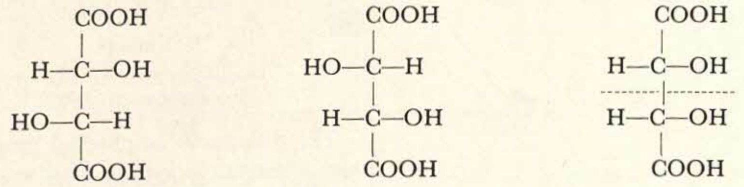
GLYCERALDEHYDE—Still another example of optical isomerism is seen in the molecules of glyceraldehyde. Both the dextrorotary and levorotary forms, illustrated here, conform to the following formulas.



$$\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{CH_2OH}\end{array}\qquad\begin{array}{c}\mathrm{CHO}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{CH_2OH}\end{array}$$

7





$$\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{COOH}\end{array}\qquad\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{HO{-}C{-}H}\\ |\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{COOH}\end{array}\qquad\begin{array}{c}\mathrm{COOH}\\ |\\ \mathrm{H{-}C{-}OH}\\ \hdashline\\ \mathrm{H{-}C{-}OH}\\ |\\ \mathrm{COOH}\end{array}$$

tartaric acid (+)
melting point 170° C

tartaric acid (−)
melting point 170° C

meso-tartaric acid
melting point 140° C

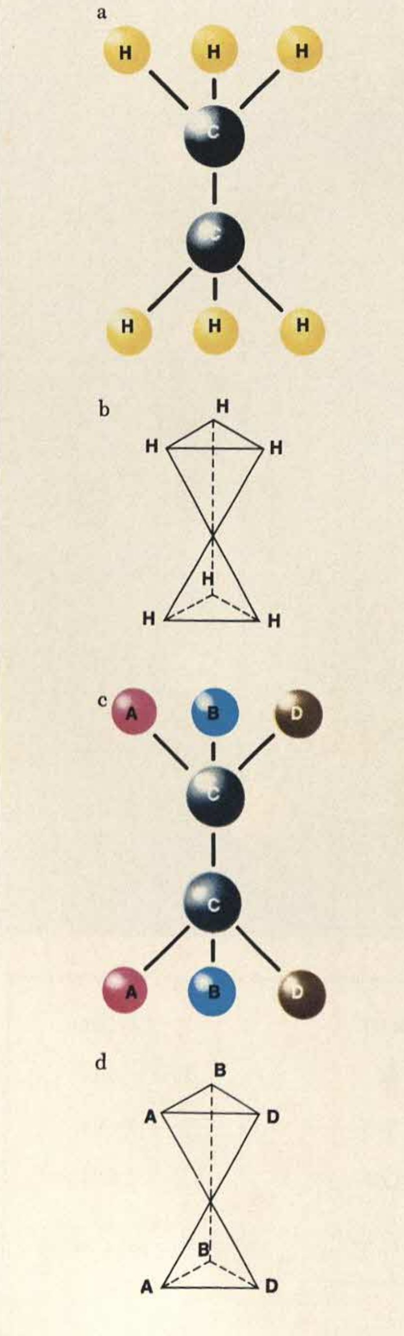
racemic tartaric acid, m.p. 206° C

STEREOISOMERISM | same formula, different structure

An important property of many compounds is that substances with the same general formula may have different molecular structures. Such substances with different molecular structures are called isomers (from the Greek *isomeres,* meaning "made of equal parts"). Thus, two structurally different compounds are said to be isomers when their molecules contain precisely the same type of atoms as well as the same number of each type of atom. The phenomenon of isomerism is very common in organic chemistry.

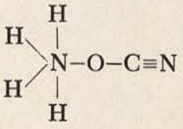
1

ETHANE AND SUBSTITUTED ETHANE—The structural formula of ethane, $CH_3—CH_3$, is shown in Illustration 1a, while Illustration 1b shows the molecule as two tetrahedrons joined at one of the vertices. In Illustrations 1c and 1d, groups **A**, **B**, and **D** have been substituted for the hydrogen atoms of the ethane molecule.



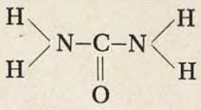
Molecules that exhibit isomerism are therefore insufficiently described by a general formula alone. For a complete understanding of the properties of such a molecule, its structure—that is, the particular way in which the atoms are bound together in space—must also be known. Differences in structure, and, therefore, differences in properties, are sometimes so marked that isomers belong to different chemical classes.

Considering a typical example, ammonium cyanate, NH_4CNO, and urea, $CO(NH_2)_2$, have the same general formula (one carbon atom, four hydrogen atoms, two nitrogen atoms, and one oxygen atom), but the atoms are bound together in different ways in the two molecules. The two compounds have very different properties. One is an inorganic salt (the ammonium salt of cyanic acid), and the other is an amide (a type of organic compound):



$$H_4N{-}O{-}C{\equiv}N$$

ammonium cyanate
decomposition
temperature = 60° C



$$H_2N{-}\underset{\overset{\|}{O}}{C}{-}NH_2$$

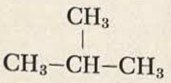
urea
melting point
= 132.7° C

There are, however, other cases in which the structural differences give rise to such small differences in physical and chemical properties that very refined methods must be used to detect them.

The aliphatic hydrocarbons butane and isobutane have the following formulas:

$$CH_3{-}CH_2{-}CH_2{-}CH_3$$

butane
boiling point = −0.5° C
melting point = −138° C

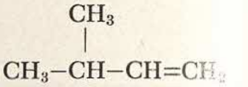


$$CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3$$

isobutane
boiling point = −12° C
melting point = −159° C

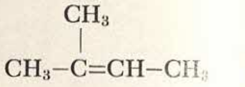
The differences in physical properties and chemical behavior between these two isomers are the result of the difference in molecular structure. Isobutane contains a three carbon atom chain with a methyl ($-CH_3$) side group, while butane is a four carbon atom chain molecule.

Another simple example of isomerism is provided by the following compounds:



$$CH_3{-}\overset{\overset{CH_3}{|}}{C}H{-}CH{=}CH_2$$

3-methyl-1-butene
boiling point = 20° C
melting point = −68.5° C



$$CH_3{-}\overset{\overset{CH_3}{|}}{C}{=}CH{-}CH_3$$

2-methyl-2-butene
boiling point = 38.6° C
melting point = −133.8° C

The compounds differ only in terms of the position of the double bond.

The isomers in the examples given contain precisely the same atoms. These atoms, or groups of atoms, however, are bonded to each other in different ways. This type of isomerism, often referred to as structural isomerism, is the most common. It is not, however, the only possible type.

It does not necessarily follow that two molecules that contain the same atoms and have the same spatial bond arrangement can be superimposed (this is merely another way of saying that the molecules are identical). In fact, the atoms can be oriented in different ways within the molecule. As a result, two different spatial configurations are possible. This type of isomerism is known as stereoisomerism (from the Greek *stereos,* meaning "solid" in the three-dimensional sense). Different types of stereoisomerism occur. In general, however, these types can be traced back to two fundamental forms—geometric isomerism and optical isomerism. The following shows the relationship between the different types of isomers.

$$\text{Isomerism}\begin{cases}\text{structural isomerism}\\ \text{stereoisomerism}\end{cases}$$

$$\text{stereoisomerism}\begin{cases}\text{geometric isomerism}\\ \text{optical isomerism}\end{cases}$$

In 1874, when he was only twenty-two years old, the Dutch chemist Jacobus van't Hoff published his classic work on the structure of the carbon atom. As a part of this work, he predicted the existence of geometric isomerism. Van't Hoff's prediction is based on the idea that there is a lack of freedom to rotate about the double bond found in unsaturated compounds. In order to explain what constitutes freedom to rotate about a bond, it is necessary to examine the structure of a saturated molecule. A suitable example is any compound derived from ethane

(C_2H_6) by means of the complete or partial substitution of other molecular groups for the ethane hydrogen atoms. Let **A**, **B**, and **D** in Illustration 1 represent different atoms or radicals that have been substituted for the hydrogen atoms in the ethane molecule. The bonds formed by the carbon atoms are arranged in the usual tetrahedral pattern. The molecule as a whole can, therefore, be represented as two tetrahedrons joined at a central vertex. Now, the bond between the two carbon atoms constitutes an axis around which the two tetrahedrons are free to rotate. The two molecules shown in Illustrations 2a and 2c do not, therefore, represent compounds different from the ones shown in Illustration 1. These are but two of the infinite number of spatial conformations possible because the two tetrahedrons are free to rotate around the axis formed by the C——C bond. This freedom to rotate disappears, however, when a double bond exists between the two carbon atoms.

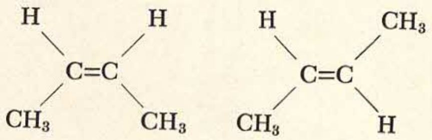
For example, consider a derivative of ethylene (Illustration 3a) in the same manner that a derivative of ethane was previously considered. As before, **A** and **B** represent atoms or radicals that have been substituted for hydrogen atoms, in this case for the hydrogen atoms in ethylene (Illustration 3b).

The configuration of the ethylene molecule is planar; that is, all of the atoms in the molecule lie in the same plane. The two carbon atoms are each situated at a vertex formed by a carbon and two hydrogen atoms. The two carbon atoms are then joined by a double bond. The molecular structure is such that the angle between any two bonds formed by a carbon atom is 120°. The six atoms in the ethylene molecule are, therefore, all situated in a single plane. The basic structure of substituted derivatives of ethylene is also planar.

It is possible to maintain the analogy with the tetrahedral structure of ethane-type compounds with their single bonds. To do this the double bond in ethylene can be shown as two curved single bonds (the model shown in Illustration 4 is often rejected, however, because it does not correspond very closely to physical reality). Pursuing this model further, molecules of derivatives of ethylene can be shown as two tetrahedrons joined along an edge. As Illustration 4 shows, the carbon atoms and atoms **A** and **B** continue to occupy positions in the same plane. This model emphasizes the fact that it is not possible to keep one tetrahedron in a fixed position and rotate the other without disrupting the line of contact between the two tetrahedrons, that is, without breaking the double bond between the two carbon atoms. This is precisely what is meant by a lack of freedom to rotate about the double bond.

Lack of rotational freedom, however, does not exclude the possibility of breaking the double bond. If the bond is broken, and then formed again after one end of the molecule has rotated 180°, the molecule that results can no longer be superimposed on the one from which it was derived. This is not the same compound, but rather its stereoisomer.

Graphical representation of the two stereoisomers presents no difficulty because the entire molecule lies in one plane. One of the two stereoisomers will have the same substituted groups on the same side of the double bond; the other stereoisomer will have different substituted groups on the same side of the double bond. The first structure is called the cis-form, the second the trans-form. Geometric isomerism is also called cis-trans isomerism. To go from the general case to a specific case, group A can be replaced by a hydrogen atom and B by a methyl group. This produces the compound 2-butene. Among the various butene isomers, this one has a linear chain with the double bond placed between the second and third carbon atoms. This molecule, therefore, can have two isomeric forms, the cis-form and the trans-form.

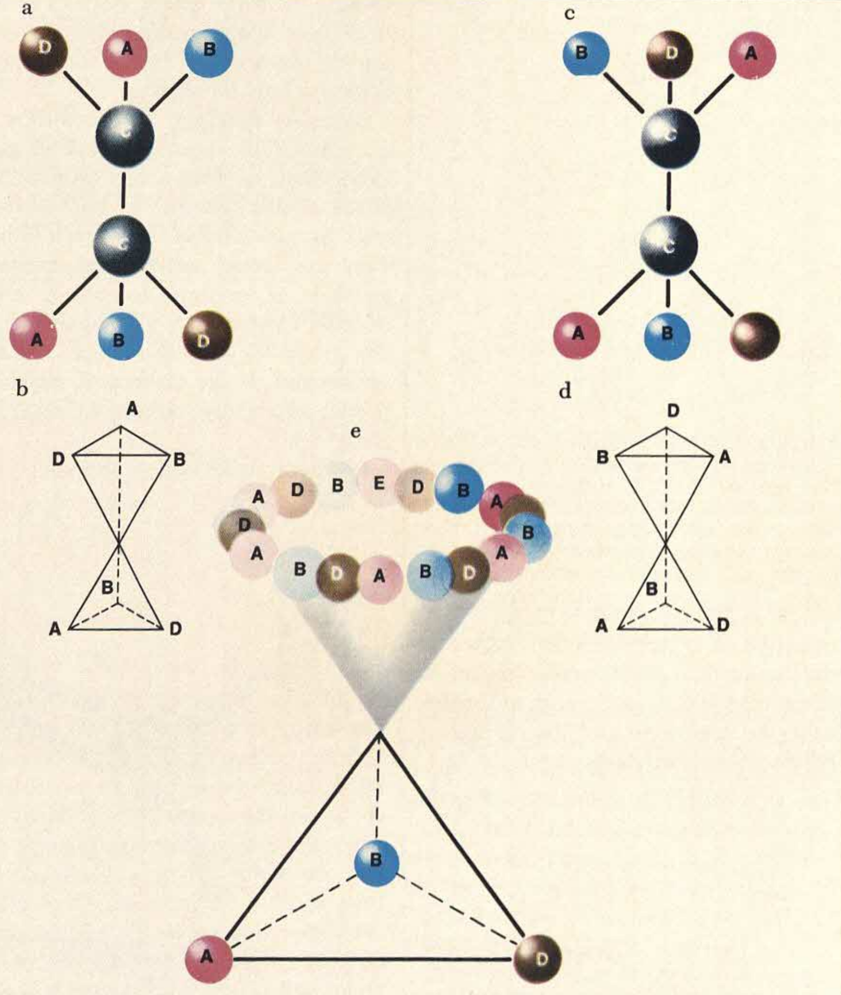


cis-2-butene
boiling point = 1° C

trans-2-butene
boiling point = 4° C

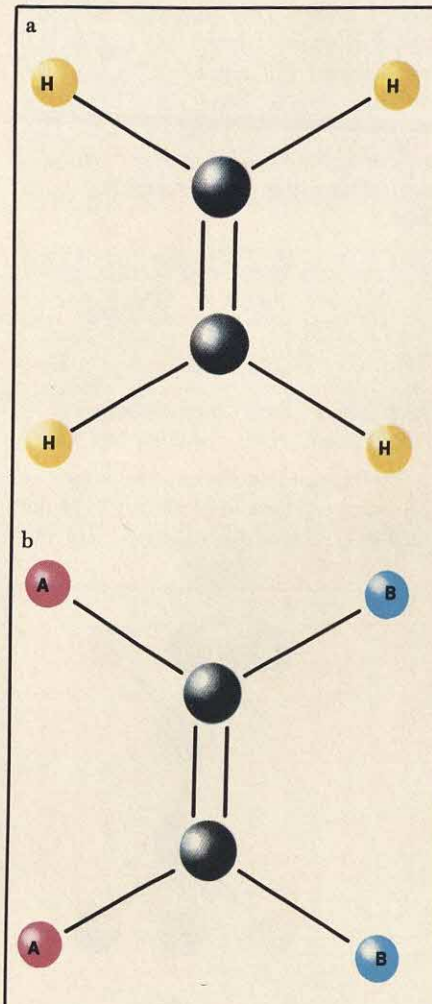
The cis- and trans-forms of a pair of geometric isomers have similar (but not identical) chemical properties, and dif-

2



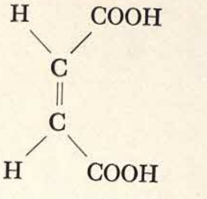
VARIOUS CONFORMATIONS OF SUBSTITUTED ETHANE—The bond between the two carbon atoms serves as an axis about which each of the two tetrahedrons is free to rotate, and can, therefore, change its position with respect to the other. The form (Illustrations 2a and 2b) is, therefore, equal to the form represented in Illustrations 2c and 2d, and both are equal to the form shown in Illustrations 1c and 1d. Finally, Illustration 2e shows that the substituted ethane molecule can assume an infinite number of conformations because either of the two tetrahedrons is free to rotate to any position with respect to the other.

3

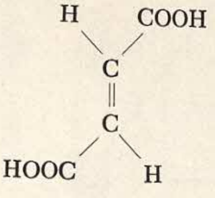


ETHYLENE AND SUBSTITUTED ETHYLENE—The ethylene molecule is planar, with the two carbon atoms joined by a double bond (Illustration 3a). The same spatial arrangement applies to the substituted ethylene (Illustration 3b), in which **A** and **B** represent any two groups substituted for the hydrogen atoms of ethylene.

ferent physical properties. Sometimes the differences are due to steric factors as is the case with fumaric acid and maleic acid, the trans-form and the cis-form of ethylene-1,2-dicarboxylic acid:

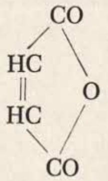


maleic acid melting point = 130° C



fumaric acid melting point = 302° C

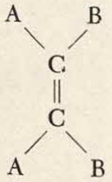
Quite apart from the considerable difference in the two melting points, it is interesting to note that maleic acid is easily converted to the cyclic anhydride by the removal of a water molecule,

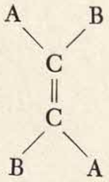


but that fumaric acid will not form such an anhydride because the two carboxylic (—COOH) groups are on opposite sides of the molecule and cannot interact. The characteristic feature of these two acids that is of interest here, however, is that, as a result of the rigidity of the double bond, the two carboxyl groups, the two remaining carbon atoms, and the two remaining hydrogen atoms are held in the same plane. (With certain nitrogen compounds, either one or two of these atoms or groups may be missing.)

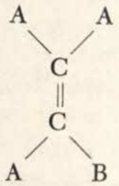
Generally speaking, the trans-form is the more stable form of a pair of geometric isomers. This occurs because adjacent similar groups in the cis-form tend to move away from each other. They are forced apart by electrostatic repulsion or for steric reasons. As a result, the trans-form of a molecule is usually produced when the double bond is synthesized. If the cis-form is required, special laboratory techniques must be employed.

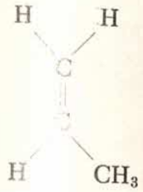
Consider these two molecules:

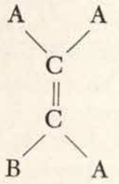


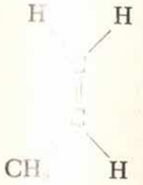


In previous examples it was specified that group A is different from group B. But now suppose that the two substituted groups on one of the two carbon atoms are the same. This produces two molecules that can be superimposed. The two molecules are now identical, and isomerism no longer exists. The following shows that geometric isomerism occurs only when each of the two carbon atoms united by a double bond is bonded to two different substituted groups:







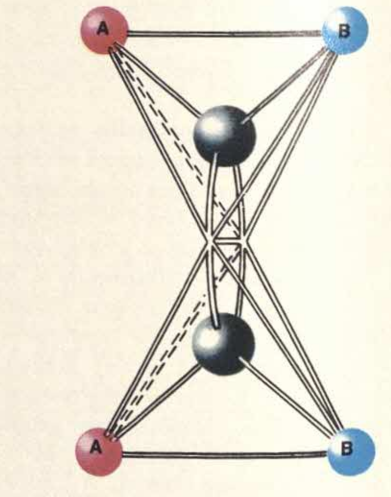


Optical isomerism, the other important form of stereoisomerism, is discussed in a separate article.

The distinction between optical and geometrical isomerism does not appear to be so significant as when it was first introduced; nevertheless, it has been retained by most chemists for historical reasons. A simple and precise definition of optical and geometrical isomerism appears to be impossible. On the one hand, many pairs of substances must be considered both optical and geometrical isomers of each other at the same time; and, on the other hand, there is no complete unanimity as to exactly where the dividing line between these two types of isomerism is to be drawn.

A UNIQUE WAY OF REPRESENTING ETHYLENE—In this model the double bond of the ethylene molecule is shown as two curved single bonds, although the model does not correspond closely to physical reality. It is obvious that neither of the tetrahedrons can rotate with respect to the other without breaking the double bond.

4



THE UNSATURATED COMPOUNDS

highly reactive and often large molecules

Ethylene, with formula $CH_2{=}CH_2$, and acetylene, $CH{\equiv}CH$, are fundamental materials from which a vast array of very important compounds are derived. These substances, the unsaturated hydrocarbons, are highly reactive and lend themselves both to interesting experimentation and numerous practical applications. The entire plastics industry, for example, owes its existence to the unsaturated hydrocarbon family.

The molecular models of ethylene and acetylene reveal immediately a characteristic differentiating them from the saturated hydrocarbons: double and triple bonds between carbon atoms. In fact, compounds derived from these sources belong to two distinct series. Those with double bonds are called ethylene hydrocarbons, also referred to as olefins or alkenes, while hydrocarbons containing triple bonds are members of the acetylene hydrocarbon series and are known as alkynes.

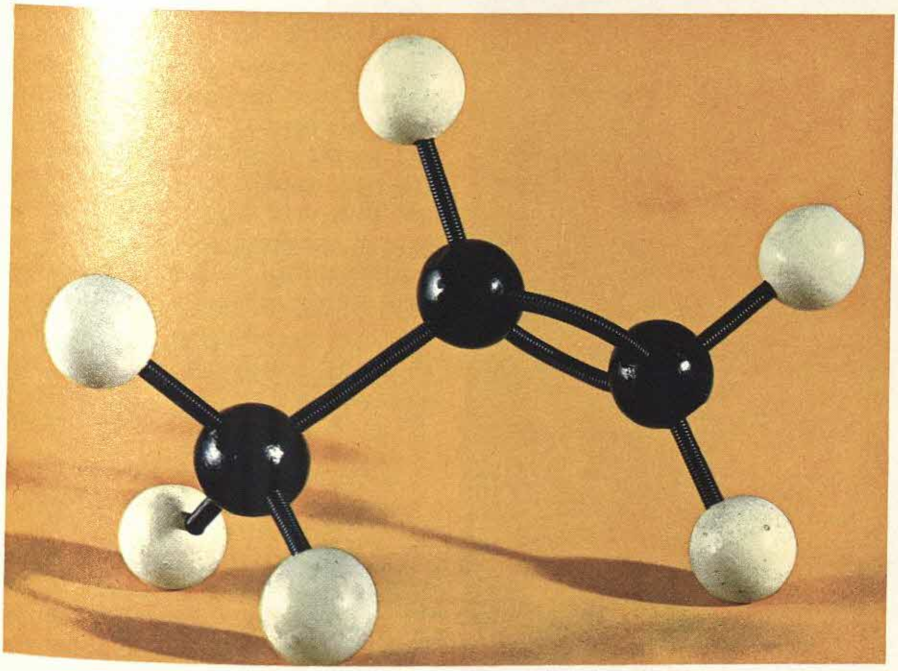
As an interesting sidelight to chemical history, the term *olefin* comes from an observation made by four Dutch chemists many years ago. These scientists succeeded in bringing about the first reaction between ethylene and chlorine, from which was produced a dense, oily liquid. This strange liquid was known for a long time as "the oil of the Dutch chemists." Now, because many compounds obtained in the same type of reaction from other ethylene hydrocarbons are also oily liquids, the entire ethylene series was dubbed olefins, meaning "oil-forming."

Today, internationally accepted nomenclature is used to identify the alkanes, alkenes, and alkynes according to these rules:

1. the *-ane* suffix denotes the saturated hydrocarbons (methane, ethane, propane, for example);
2. the *-ene* suffix indicates an unsaturated hydrocarbon with a double bond (propene, for example);
3. the *-yne* suffix signifies unsaturated hydrocarbons having triple bonds (propyne, for example).

PROPENE—This is the second member of the hydrocarbon series in which the compounds contain double bonds. Propene finds importance as an intermediary in the production of plastics, especially polypropylene.

1



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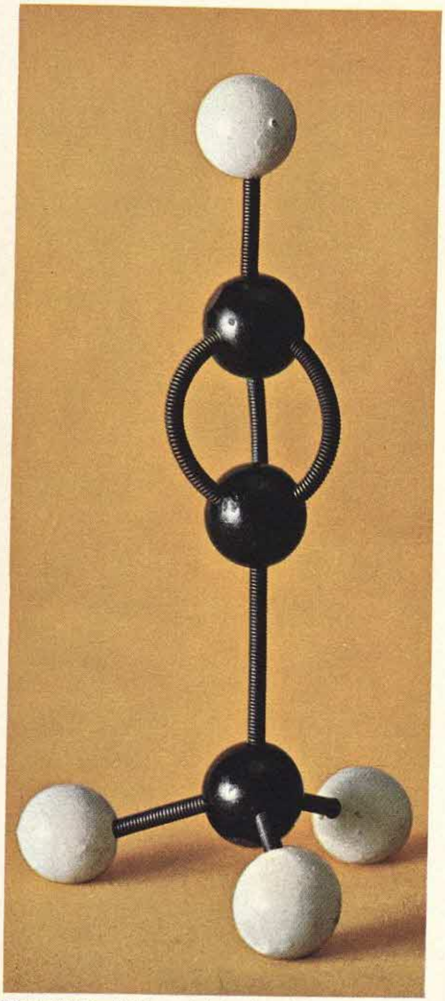


PROPYNE—With a triple bond in its molecule, propyne is the second member of the alkyne series. Unlike the molecules with double bonds, the alkynes are of little industrial importance. In fact, only acetylene enjoys any distinction in this regard.

The primary industrial source of ethylene hydrocarbons is the petroleum industry, from which they are obtained in the cracking of crude oil (cracking is the process by which molecules are split into two or more fragments by heat). In this manner, large quantities of the important "lower" olefins (those with few carbon atoms) are obtained.

Ethylene, the first of the alkene series, is used as the starting point in the synthesis of such valuable compounds a ethyl alcohol, and as a component in the production of plastics. Another example of the importance of the alkenes is provided by propene (propylene), $CH_3-CH=CH_2$, the next member of the family. This compound is best known for its use in plastic technology and numerous other organic syntheses.

With the exception of acetylene, well known as the gas used in steel-cutting torches, the alkynes are little used industrially. Moreover, because of their extreme reactivity they are rarely found in nature. In the laboratory, however, the hydrocarbons with triple bonds are quite useful as synthetic intermediates.

REACTIVITY

The high level of reactivity is due directly to the unsaturated state of carbon bonds in the alkenes and alkynes. The reactions involving unsaturated hydrocarbons can be roughly divided into two classes: cleavage reactions and addition reactions. Cleavage reactions, wherein the double or triple bonds are literally broken, are particularly interesting when the desire is to ascertain molecular structure. To do so simply means breaking the molecule into smaller, more easily recognizable fragments. When these fragments are identified, it is often possible to deduce the structure of the original molecule.

One of the more frequently used methods of degrading a molecule employs ozone. This molecule, O_3, is distinguished from its life-giving relative, O_2, by greater reactivity and the ease with which it becomes attached to double and triple bonds.

The alkenes and alkynes react with ozone to yield, depending on the compound and the reaction conditions, aldehydes, ketones, or acids, all of which are easily recognized. From these, original molecules can be reconstructed.

The use of ozone and other methods of degradation are valuable research tools widely applied in the study of organic structures. On the other hand, for purposes of organic synthesis addition reactions are far more important. In these reactions, the addition of other atoms or groups always occurs on the two carbon atoms between which the double or triple bonds occur. Furthermore, addition always leads to the formation of less highly unsaturated compounds.

Undoubtedly, the simplest example of an addition reaction is that of the formation of alkanes by the addition of hydrogen to alkenes and alkynes. This important process is called hydrogenation. A catalyst is required to make the addition take place, and this generally takes the form of powdered nickel, platinum, or palladium. The following equations illustrate the mechanism:

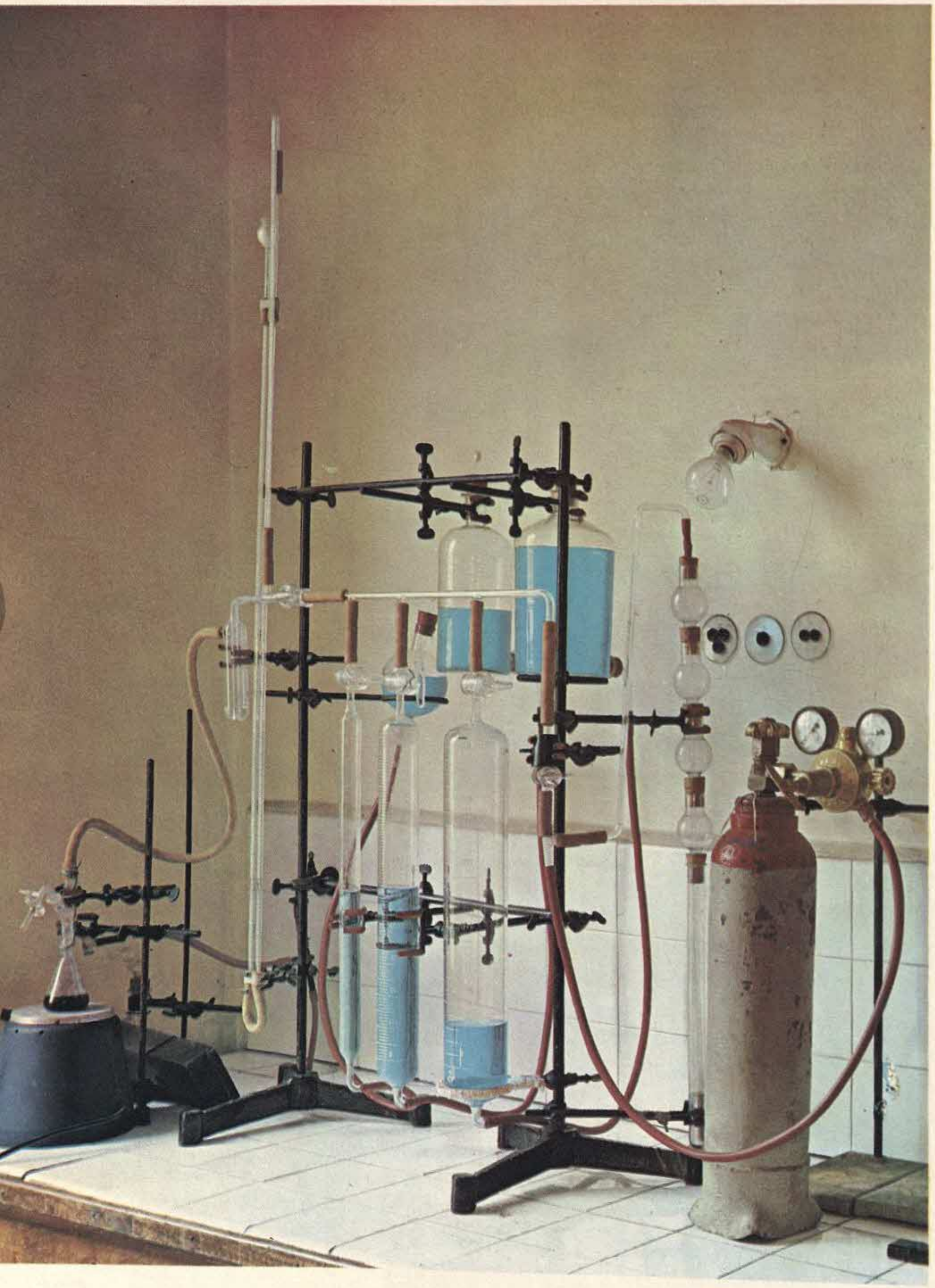
$$>C=C< + H_2 \xrightarrow{Ni} H-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-H$$

$$-C\equiv C- + 2H_2 \xrightarrow{Ni} H-\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}-H$$

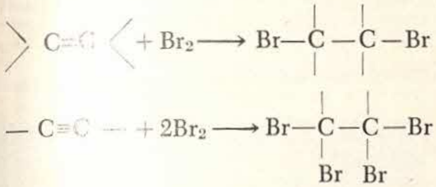
One of the many applications of the hydrogenation reaction is seen in the hardening of oils. A valuable industry is based on the transformation of fish and vegetable oils—liquids of little commercial value—into marketable solid fats. One of the most worthy products is margarine, which provides a low-cost source of fat necessary in the human diet.

HYDROGENATION—This apparatus, valuable in organic chemistry, accommodates hydrogenation reactions. In these reactions, hydrogen atoms are added to unsaturated compounds, generally in the presence of a nickel, platinum, or palladium catalyst.

3



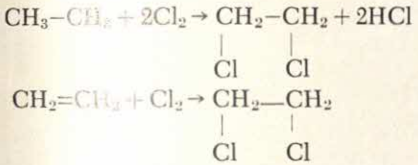
The halogens and their acids represent other substances that are readily added to unsaturated bonds. In these instances, the products are chlorinated solvents and some insecticides.



$$>C=C< + Br_2 \longrightarrow Br-\overset{|}{\underset{|}{C}}-\overset{|}{\underset{|}{C}}-Br$$

$$-C\equiv C- + 2Br_2 \longrightarrow Br-\overset{|}{\underset{Br}{C}}-\overset{|}{\underset{Br}{C}}-Br$$

At this point, it must be noted that halogenation by addition to unsaturated bonds differs substantially from halogenation reactions with saturated compounds, even though the same products often obtain. In fact, alkanes are subject only to substitution reactions, where one or more hydrogen atoms are replaced by halogen atoms. Compare these reactions:

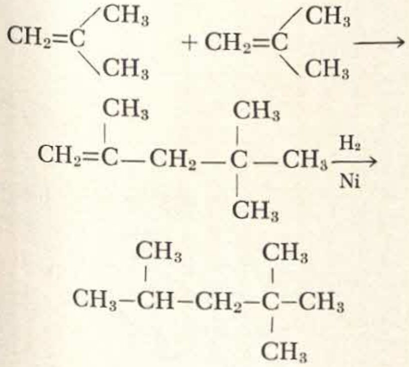


$$CH_3-CH_3 + 2Cl_2 \rightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH_2} + 2HCl$$

$$CH_2=CH_2 + Cl_2 \rightarrow \underset{Cl}{CH_2}-\underset{Cl}{CH_2}$$

In qualitative analysis, the addition of bromine to a hydrocarbon quickly establishes whether or not the compound is unsaturated. Elemental bromine has an intense red color, and solutions containing it remain reddish even in extreme dilution. Mixed with an unsaturated hydrocarbon, the bromine reacts and the color disappears. This is not the case with saturated hydrocarbons. It must be stressed that such a test is only qualitative, and then only in a limited way, for a few unsaturated compounds do not react with bromine—and some organic compounds are not hydrocarbons at all, but do react with bromine. Nevertheless, such tests can serve as guideposts.

One of the most important alkene addition reactions is that of the dimerization of isobutylene. When dissolved in sulfuric acid and heated for one minute at 100° C (212° F), isobutylene becomes an isooctene, and from this is obtained isooctane via hydrogenation.

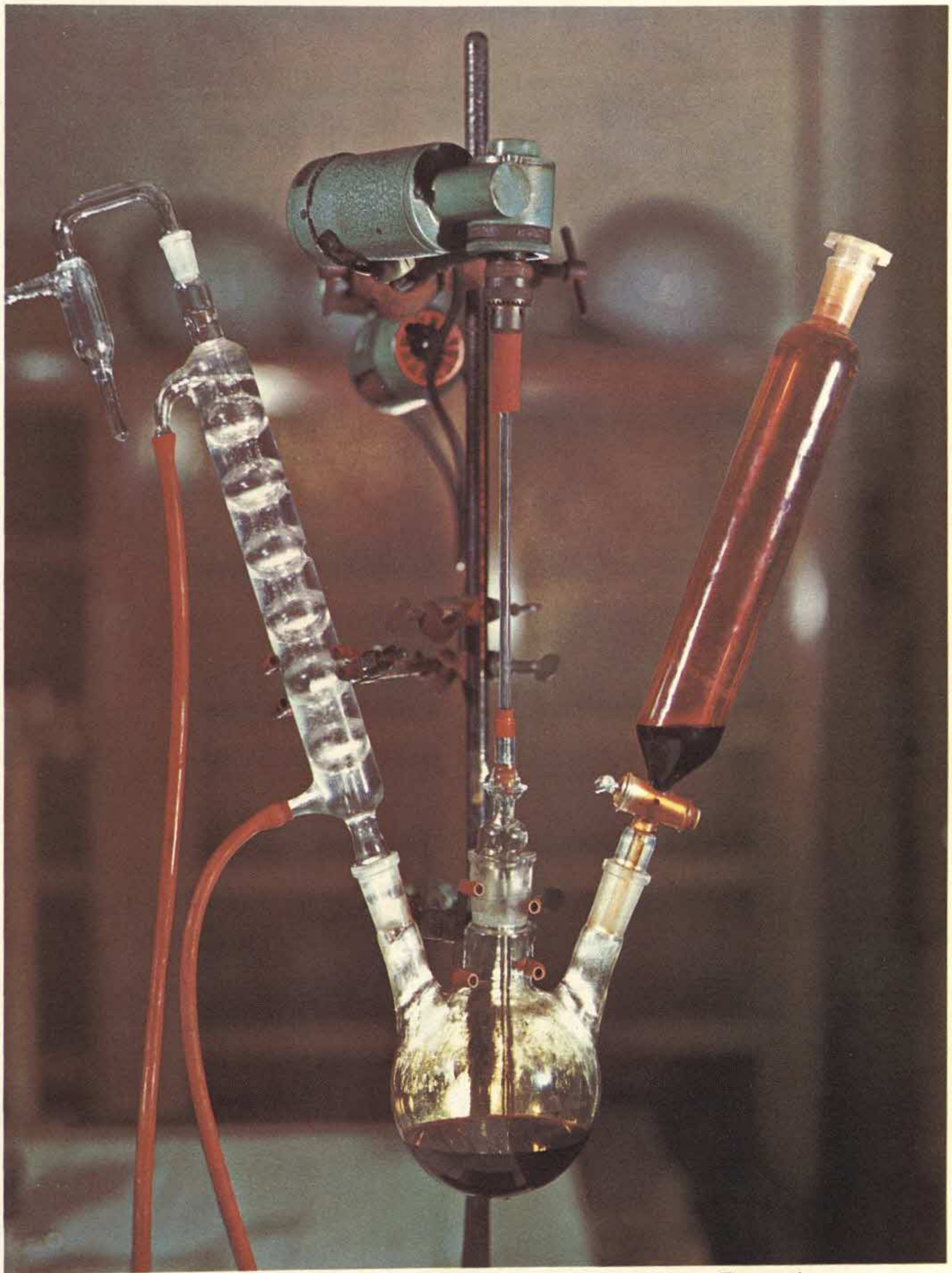


$$CH_2=C\begin{matrix}CH_3\\CH_3\end{matrix} + CH_2=C\begin{matrix}CH_3\\CH_3\end{matrix} \longrightarrow$$

$$CH_2=\overset{CH_3}{\overset{|}{C}}-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3 \xrightarrow[Ni]{H_2}$$

$$CH_3-\overset{CH_3}{\overset{|}{CH}}-CH_2-\overset{CH_3}{\overset{|}{\underset{\underset{CH_3}{|}}{C}}}-CH_3$$

4

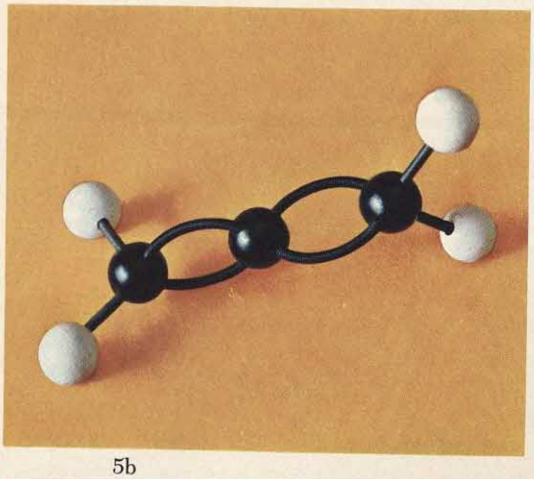


BROMINATION—Halogens such as bromine are easily added to unsaturated compounds, and this leads to a host of new materials with numerous practical applications. The equipment shown here is used in the laboratory for performing a bromination reaction.

Isooctane is of tremendous importance to the automotive industry. When used as a motor fuel, isooctane displays excellent antiknock properties. By definition, isooctane has an octane number of 100, and is the basis for designating all fuels in terms of octane rating. Thus, when a given fuel is said to have an octane rating of 80, its antiknock characteristics are the same as those of a mixture containing 80 parts isooctane and 20 parts n-heptane (whose octane number is zero, also by definition).

The tendency of the lower alkene molecules to become added to one another, under the influence of certain catalysts, with the formation of long polymer chains, represents another aspect of the reactivity of double bonds. In particular, two polyolefins are of outstanding indus-

5a



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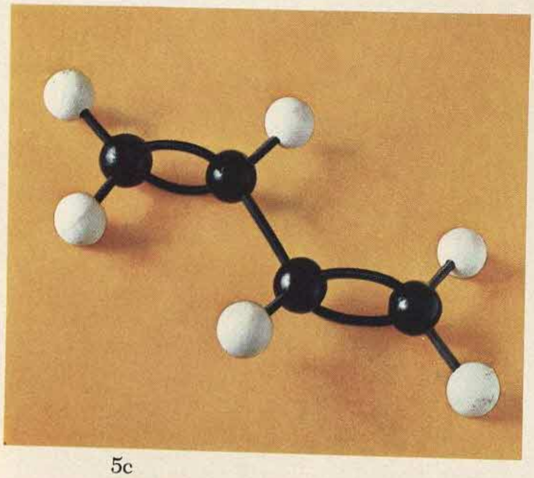
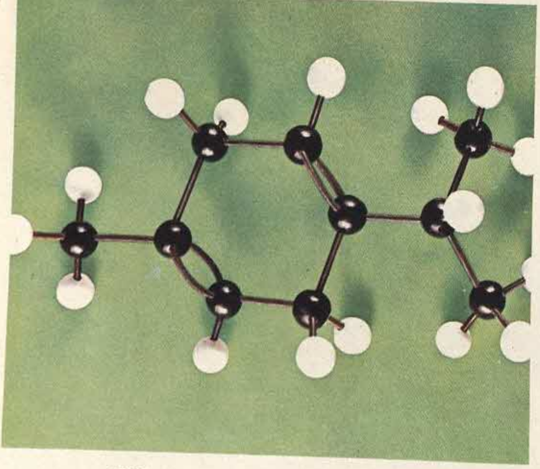


5c



DIENES—The dienes are a series of compounds characterized by two double bonds in the molecule. Illustration 5a shows the structure of allene, the first member of the series. Butadiene-1,3, shown in Illustration 5b, is one of the most important intermediates in the manufacture of synthetic rubber. The complex molecule in Illustration 5c represents one of the cyclic dienes, and is typical of those found in plant oils.

trial importance. These are polyethylene and polypropylene.

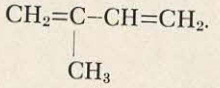
DIENES

This type of organic compound is characterized by molecules that contain more than one double bond. Specifically, those containing two double bonds give the name to the entire species, the dienes.

The dienes are further classified into three groups according to the positions of the double bonds within the molecule. Those compounds having adjacent double bonds are the allenes, with the first member of the group being propadiene, $CH_2{=}C{=}CH_2$. Next, if the double bonds are separated by a single bond, the compounds are called conjugated dienes. Last are the isolated dienes in which the pair of double bonds is separated by more than one single bond.

Of the three groups, the conjugate dienes are the most important for several reasons: they are very reactive; they are structurally related to a large number of natural substances; and, they have many industrial applications.

The first and simplest member of the series is butadiene, $CH_2{=}CH{-}CH{=}CH_2$. Its most notable derivative is isoprene, or 2=methyl=1,3=butadiene,



$$\begin{array}{l} CH_2{=}\underset{\displaystyle |\atop \displaystyle CH_3}{C}{-}CH{=}CH_2. \end{array}$$

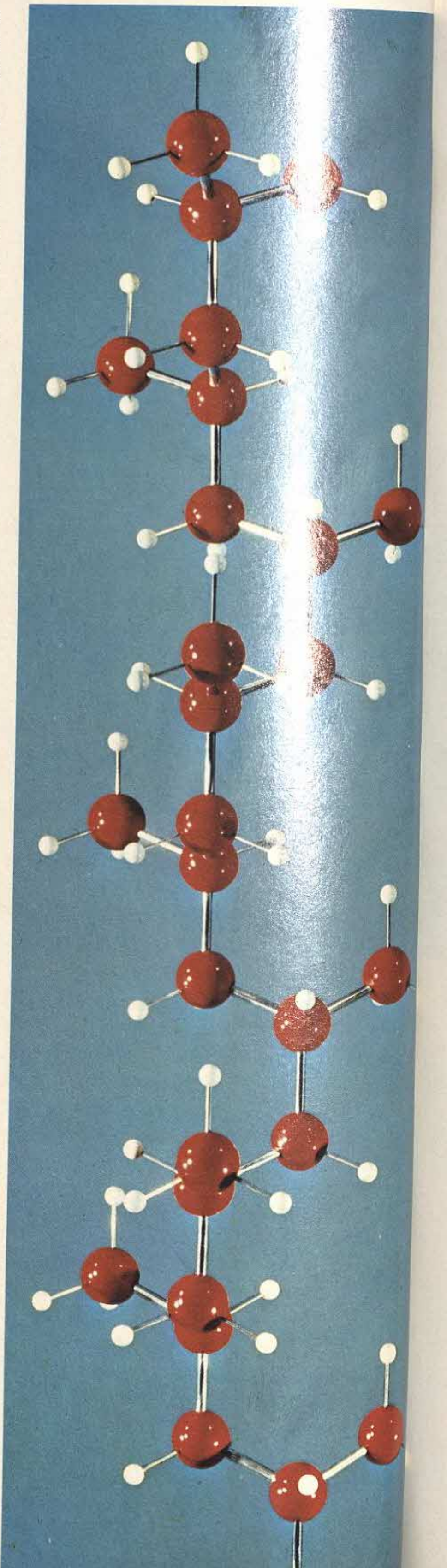
A striking feature of the diene synthesis is the ease with which it can be effected without the use of powerful chemical reagents. Study of the reaction has contributed greatly to the knowledge of polymerization processes by which valuable plastics have been obtained.

The isoprene skeleton appears in many natural substances; the prime example is natural rubber. Originally, this substance was thought to be formed from five or ten isoprene molecules condensed into a ring. It is now realized that the structure of natural rubber consists of hundreds of linearly polymerized isoprene molecules.

Because isoprene is so widely spread in nature, many natural compounds have carbon atoms numbering in multiples of five. In fact, observation of their structures indicates derivation from the union of several isoprene molecules.

ISOTACTIC POLYPROPYLENE—Since there is no limit to the number of alkene molecules that can be added together, the chemical industry has created macromolecules. Just such a compound is isotactic polypropylene (isotactic refers to the fact that all the methyl groups are on the same side of the chain). A chain of this synthetic material can, in practice, be prolonged indefinitely simply by a succession of polymerization reactions.

6

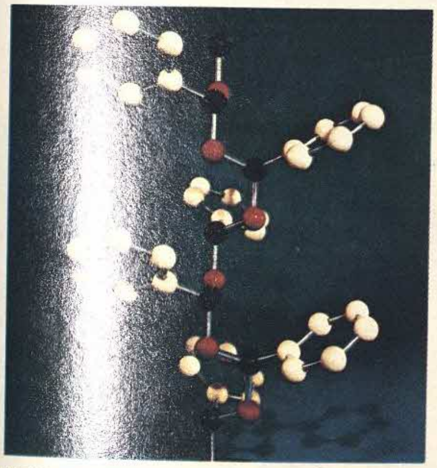


THE POLYMERS

chemistry of the macromolecules

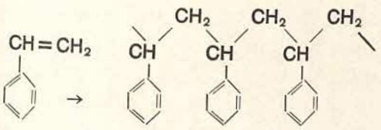
Although macromolecular chemistry is a relatively new field of research, it has already attained great importance and sophistication. Polymers are macromolecules that consist of repeating units (monomers) and that have an enormous range of practical applications. They are used in adhesives, utensils, satellites, and space suits. Certain synthetic textile fibers and various plastic and synthetic rubber products are made up of polymers.

All polymers have high molecular weights; they are formed by the union of many small, fundamental units (monomers). The number of monomers uniting defines the degree of polymerization of the resulting substance. Polymers, therefore, may be classified by their molecular weight: low polymers are those with a molecular weight of less than 1,000; medium polymers have a molecular weight of from 1,000 to 10,000; high polymers can reach a molecular weight of around 1,000,000.



MOLECULAR MODEL OF AN ISOTACTIC POLYSTYRENE—If the monomer units of a polymer chain are arranged according to a certain rule, the polymer is said to be tactic, from the Greek meaning "put in order." If there is no spatial ordering of the units, the polymer is said to be atactic. Isotactic and syndyotactic polymers are types of tactic polymers. A polymer is isotactic if the monomer units are asymmetrical and arranged in such a way that any two successive units (subject to rotation and translation) can be exactly superimposed.

In syndyotactic polymers, an appropriate rotation and translation of any one unit must turn that unit into a mirror image of the next unit. Polystyrene is formed by polymerization of styrene:



Polystyrene has a low specific weight and is worked easily; however, it is highly flammable.

Polymers are formed by condensation or addition reactions. In condensation reactions, the binding together of monomers is accompanied by the elimination of secondary substances. Polymerization by addition always involves unsaturated molecules and the resulting polymers have a molecular weight that is an exact multiple of the molecular weight of the basic monomer.

Monomers and polymers are represented as:

$$\begin{array}{cr} -M- & (\text{monomer}) \\ M-M-M-M-M & (\text{polymer}). \end{array}$$

If a polymer is made up of n monomers, it is represented as:

$$(-M-)_n,$$

where n is the degree of polymerization.

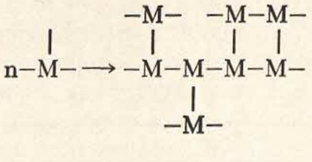
In practice, not all the molecules of a polymer have exactly n units and the molecular weight is, therefore, always an average—or statistical—weight.

For molecules to polymerize, they must have at least two atoms (or groups of atoms) capable of entering the reaction. Without two reactive sites, only dimerization can occur:

$$M- + -M \longrightarrow M-M.$$

With two reactive sites, the resulting polymer is a linear macromolecule—a chain of polymers in which the head of one monomer is joined to the tail of another (this is the kind of polymer that yields fibers).

With three reactive sites on each monomer, three-dimensional polymers are obtained:



$$\begin{array}{ccccccc} & & -M- & & -M & - & M- \\ | & & | & & | & & | \\ n-M- & \longrightarrow & -M & - & M & -M- & M- \\ & & & & | & & \\ & & & & -M- & & \end{array}$$

A copolymer is one formed by the union of two or more different monomers. The monomers are arranged along the chain, their position depending on their reactivity and the conditions of copolymerization (percentage of monomers, or solvent, are contributing factors). A random succession could result:

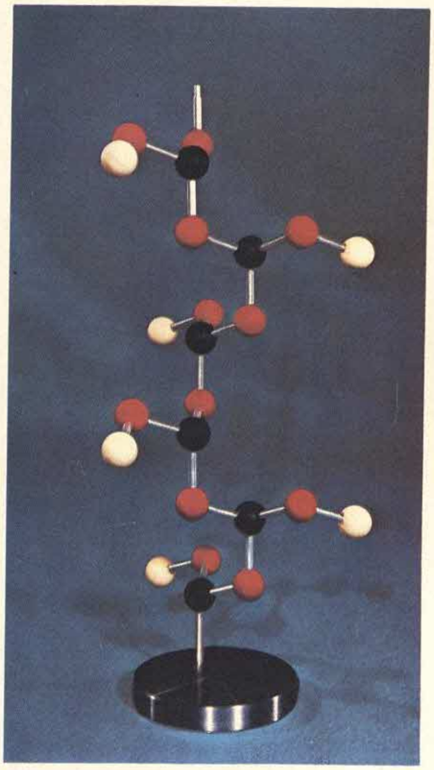
$$\begin{array}{l} -C- + -D- \\ \rightarrow -C-D-D-D-C-C-D-C-, \end{array}$$

or a succession of alternate monomers, or monomers with a block or bridge arrangement. The properties of a copolymer depend on many factors. By changing the conditions of polymerization, products with different properties can be obtained.

Heteropolymerization is an addition polymerization. Two or more molecular species are involved, one of which will not polymerize by itself. Usually a double or triple bond is needed in the monomer's structural formula in this process to form units in high polymers.

POLYMERIZATION BY CONDENSATION

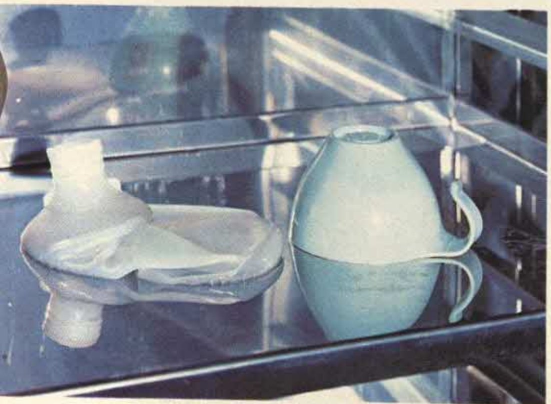
Monomers are condensed by the elimination of simple molecules (such as water). A condensation of this type leads to the most important product in food packag-



MOLECULAR MODEL OF AN ISOTACTIC POLYALPHA BUTENE—This polymer (and others of the polyalpha olefin series) are presently the subject of extensive research.

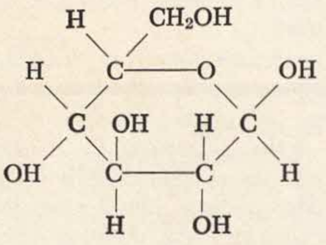
THERMAL HARDENING AND THERMOPLASTICITY—A three-dimensional polymer is derived from monomers with three active sites. Each molecule of the polymer can have reactive centers. In an early stage of polymerization, such a polymer is soluble in common solvents and will soften and fuse when heated. The molecules in the fused state react with each other, increasing the molecular weight. The polymer thus hardens in an irreversible manner, becoming insoluble and unfusible. Such polymers are said to be thermohardened.

Polymers without reactive sites cannot create bonds between the chains. These, therefore, remain soluble and melt on being heated. The illustration shows a bottle made from a thermoplastic material and a cup made of thermohardened material. The cup can be used as a container for hot liquids; the bottle cannot.

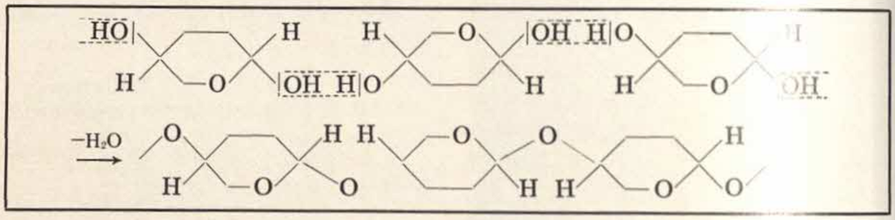


THE EFFECT OF HEATING—A thermohardened article is made by heating thermohardening molding powders, which have a low degree of polymerization. The powder softens and can be molded into the desired shape. The object produced is then hardened by being kept at a certain temperature for a time. Thermoplastic molding powders are heated to fluidity in a mold and then allowed to cool. The properties of these two kinds of objects are different, as shown in the illustration. The heated bottle has softened; the cup is unaffected.

ing: cellulose, a polymer in which glucose is the monomer:



The formation of cellulose polymers from glucose is represented as follows:



The paper industry and artificial textile fiber industry are based on cellulose.

Artificial fibers are made from polymers that already exist in nature. Synthetic fibers are those wholly produced by chemical synthesis. Man-made fibers are used separately, together as blends, or in combination with natural fibers.

One of the most important synthetic polymers is nylon, in all its various forms, such as nylon 6, nylon 6,6, and nylon 10. Nylon 6 has six carbon atoms in the lactam that is its starting monomer. Nylon 6,6 is obtained by condensation of hexamethylenediamine and adipic acid (the numbers 6,6 indicate the six carbon atoms of the diamine and the six of the acid).

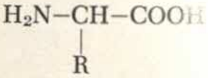
$$H\boxed{_2}N(CH_2)_6NH\boxed{_2}\quad \boxed{HO}OC-(CH_2)_4-CO\boxed{OH}\quad H\boxed{_2}N(CH_2)_6NH\boxed{_2}\longrightarrow$$
$$-HN(CH_2)_6NH-CO-(CH_2)_4-CO-NH-(CH_2)_6-NH----$$

Nylon 10 is obtained from the polycondensation of the amine of undecanoic acid, $H_2N-(CH_2)_{10}-COOH$, which polymerizes as follows:

$$nNH_2-(CH_2)_{10}-COOH$$

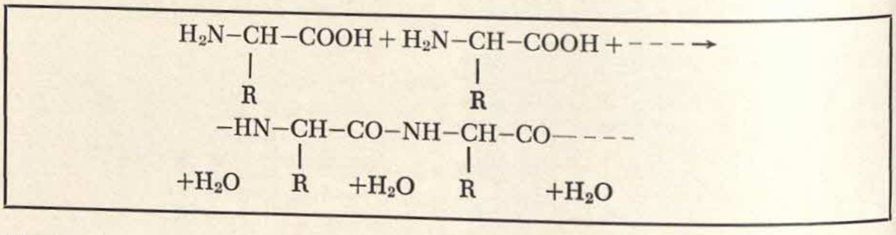
$$\rightarrow \underset{+H_2O}{NH-(CH_2)_{10}-CO}-\underset{+H_2O}{NH-(CH_2)_{10}-CO}$$

Wool and silk are natural fibers of animal origin. Their fundamental constituents are the amino acids. The general formula for an amino acid is



$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH$$

where R represents a group or lateral chain that specifies the amino acid. Amino acids condense to form polypeptides, the protein macromolecules that form the basis for all living organisms:

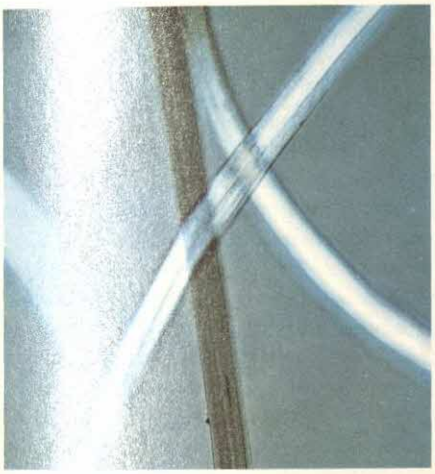


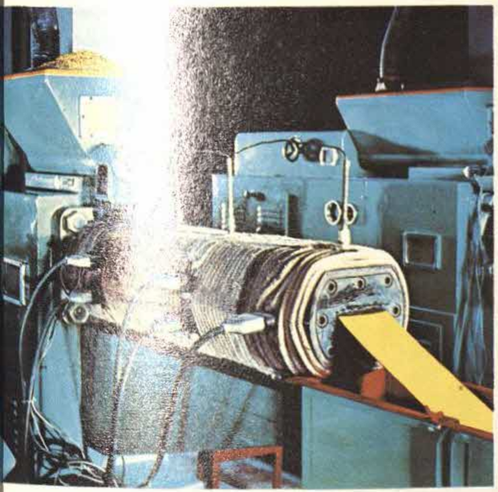
$$H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH+H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH+---\rightarrow$$
$$\underset{+H_2O}{-HN}-\underset{\displaystyle R}{\underset{|}{CH}}-\underset{+H_2O}{CO-NH}-\underset{\displaystyle R}{\underset{|}{CH}}-\underset{+H_2O}{CO}----$$

Wool polymers contain the amino acid cystine, which is not found in silk. Seventy percent of silk fibers are made up of amino acid monomers, for which R=H or CH_3. These monomers are not found in wool.

In condensation polymerization reactions, the monomers are mixed with the catalyst—if any is required—in an aqueous medium or in particular solvents such as ethyl alcohol. Appropriate equipment, temperature, and pressure must be applied. It is possible also to fuse the mixture of monomers and catalyst and

POLYVINYL CHLORIDE FIBERS—Polyvinyl chloride is obtained by polymerizing vinyl chloride in the presence of suitable catalysts (peroxides or persalts). The starting product is methane, with acetylene and vinyl chloride as intermediate products. Ethylene also can be used as a raw material, with dichloroethane and vinyl chloride as intermediate products. The photograph shows polyvinyl fibers in polarized light. (250 X)





EXTRUSION—Extrusion is the process that turns the molding powders into threads, tubes, laminas, and similar linear forms. The photograph shows extrusion of a colored plastic sheet, from molding powder contained in the hopper.

carry the reaction into the gaseous state.

POLYMERIZATION BY ADDITION

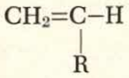
Monomers that polymerize by addition are molecules with weak linkages. The olefins, which contain the double bond C=C, are an example. The double bond is activated at lower energy thresholds, thus opening more easily and enabling the monomers to join together in a long chain. Another example is ethylene. When heated under pressure in oxygen, ethylene yields a compound called polyethylene whose degree of polymerization can be as high as 20,000.

$$nCH_2{=}CH_2 \xrightarrow[\text{pressure}]{O_2\text{ heat}} n{-}CH_2$$

$$\longrightarrow -CH_2-CH_2-CH_2-CH_2-$$

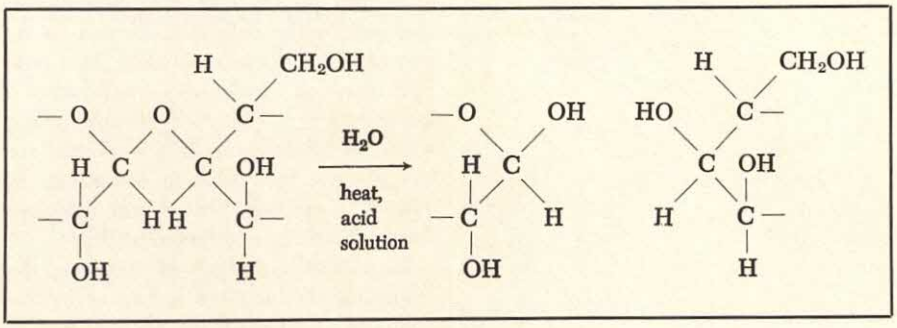
This polymer (commonly known as polyethylene) is used in cable insulations and in many domestic and industrial products.

The polyvinyls are another important class of polymers. These contain the vinyl group $CH_2{=}CH-$. The general formula for the monomer is

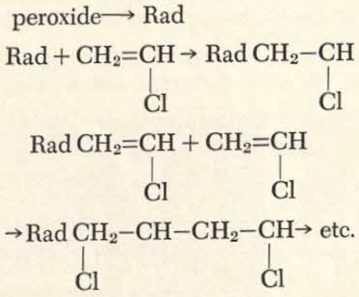


$$CH_2{=}\underset{\displaystyle R}{\underset{|}{C}}{-}H$$

where the R group is the distinguishing factor. R can be a halogen or a radical such as $-CN$ or $-C_6H_5$.



Almost all addition polymerization reactions need a catalyst to initiate the reaction. The polyvinyl chloride reaction uses peroxide, which is transformed into a free radical (a group containing an unpaired electron) and initiates a chain reaction



$$\text{peroxide} \longrightarrow \text{Rad}$$

$$\text{Rad} + CH_2{=}\underset{Cl}{\underset{|}{CH}} \rightarrow \text{Rad}\,CH_2{-}\underset{Cl}{\underset{|}{CH}}$$

$$\text{Rad}\,CH_2{=}\underset{Cl}{\underset{|}{CH}} + CH_2{=}\underset{Cl}{\underset{|}{CH}}$$

$$\rightarrow \text{Rad}\,CH_2{-}\underset{Cl}{\underset{|}{CH}}{-}CH_2{-}\underset{Cl}{\underset{|}{CH}} \rightarrow \text{etc.}$$

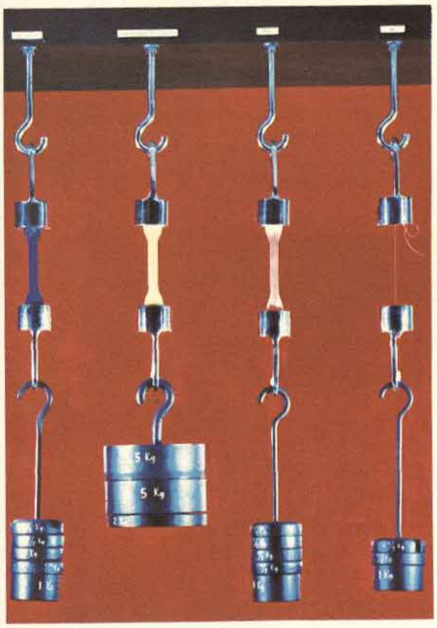
These reactions can be catalyzed also by Lewis acids (giving rise to carbon cations), or by light (giving rise to free radicals). Polyvinyl chloride is used to make paints and phonograph records.

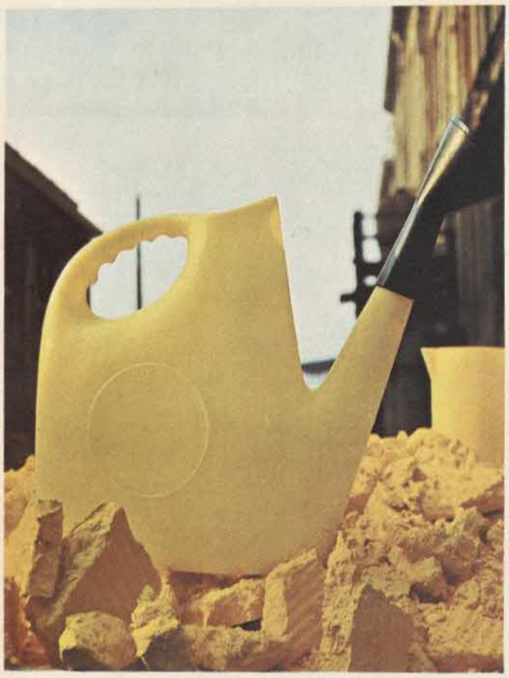
Another important polymer formed by addition is polypropylene. The monomer for this is propylene $CH_3-CH-CH_2-$.

Addition polymerization reactions can be carried out in a fused (monomer and catalyst) state, in a gaseous state, in solution, or in suspension.

Polymers are substances of great variety and usefulness and occur widely in modern living. Although most are highly durable in use, they are subject to degradation.

TENSILE TESTS OF POLYPROPYLENE—Isotactic polypropylene has a melting point in the neighborhood of 170° C (338° F) and can be used up to 140° C (284° F) without undergoing alteration. It is an excellent dielectric and has high tensile strength and surface hardness. The illustration shows threads of various diameters and types being tested in tension. Polypropylene is used in textile fibers and film.

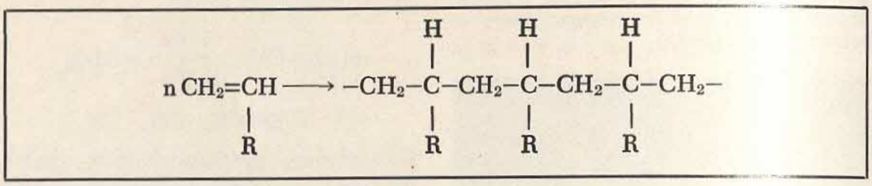




THE APPEARANCE OF ISOTACTIC POLYPROPYLENE—The two articles in the illustration are resting on blocks of unmolded polypropylene, similar to those from which they were made.

DEGRADATION OF POLYMERS

Degradation is the breakdown of a polymer chain by physical or chemical action, reducing the degree of polymerization. An example is the hydrolytic degradation of cellulose. When this natural polymer is heated in an acid solution it hydrolyzes, with a breakdown of the oxygen bridge bond.



$$n\,CH_2{=}\underset{\overset{|}{R}}{CH} \longrightarrow -CH_2-\overset{\underset{|}{H}}{\underset{\overset{|}{R}}{C}}-CH_2-\overset{\underset{|}{H}}{\underset{\overset{|}{R}}{C}}-CH_2-\overset{\underset{|}{H}}{\underset{\overset{|}{R}}{C}}-CH_2-$$

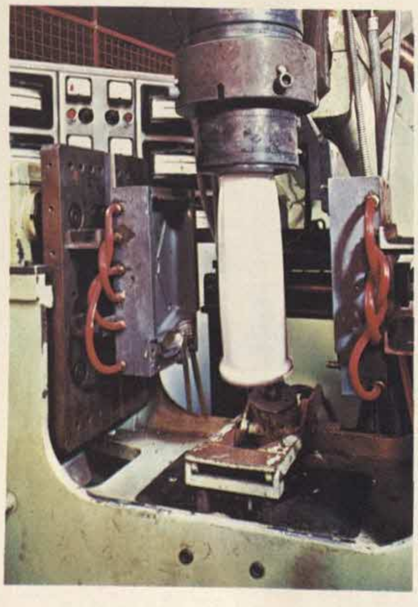
If carried to the limit, this degradation can reduce the cellulose polymer to its constituent glucose monomers. In a true homogeneous hydrolysis, however, a quantitative recovery of glucose is not observed since there is a tendency for the glucose molecules to recombine to reform a polymer that is not cellulose but is definitely a polysaccharide.

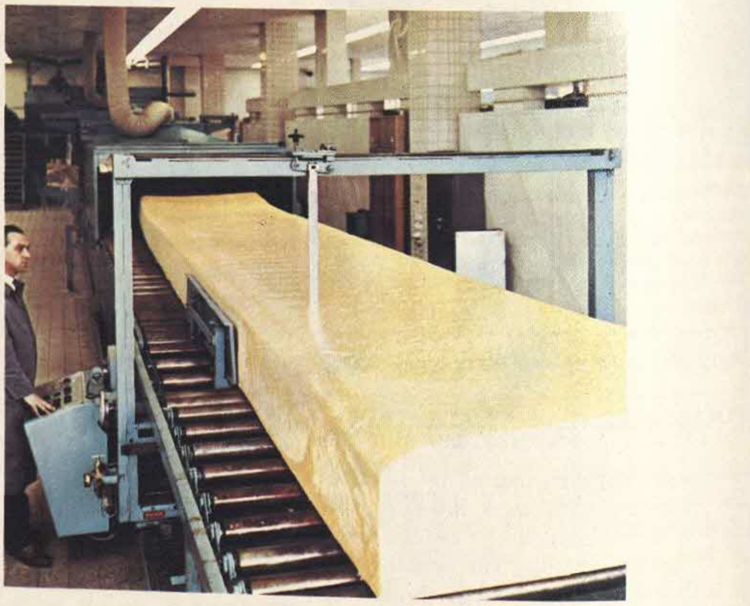
In partial hydrolysis of cellulose, the degraded products are known as hydrocellulose. A wide variety of these can be prepared; their properties are determined by the conditions of the hydrolytic treatment. In general, degradation of cellulose by acids is accompanied by a decrease in viscosity and in tensile strength, by an increase in reducing power, and in solubility in aqueous alkalies. Cellulose can be degraded also by oxidizing agents, by mechanical action, by heating, and by various organisms. Many bacteria, fungi, and protozoa cause decomposition of cellulose with the ultimate production of carbon dioxide and water.

While a slight depolymerization of cellulose is permissible in the production of artificial fibers, degradations are almost always harmful because the physical and mechanical properties of polymers (such as strength and pliability) are closely related to the chain length.

EXTRUSION OF BASKETS—The photograph shows an extrusion machine making polypropylene baskets. The polymer becomes homogenized as it passes through regions of the machine where appropriate temperatures and pressures are maintained. The fused mass is then forced through the orifice and extruded in the form desired.

THE PRODUCTION OF MULTIPRENE—Multiprene, an expanded polyurethane, is shown in the illustration. It is obtained by first preparing a polymer of low molecular weight with free isocyanic groups (–NCO) and then condensing it in the presence of water. Carbon dioxide is released in the process.





GIANT MOLECULES | the synthesis of polymers

Macromolecular substances are the result of continuous reactions among simple molecules. These substances are developed from chain reactions among molecules that have particular characteristics of reactivity. Many macromolecular substances are found in nature: natural rubber, wool, silk, and cellulose.

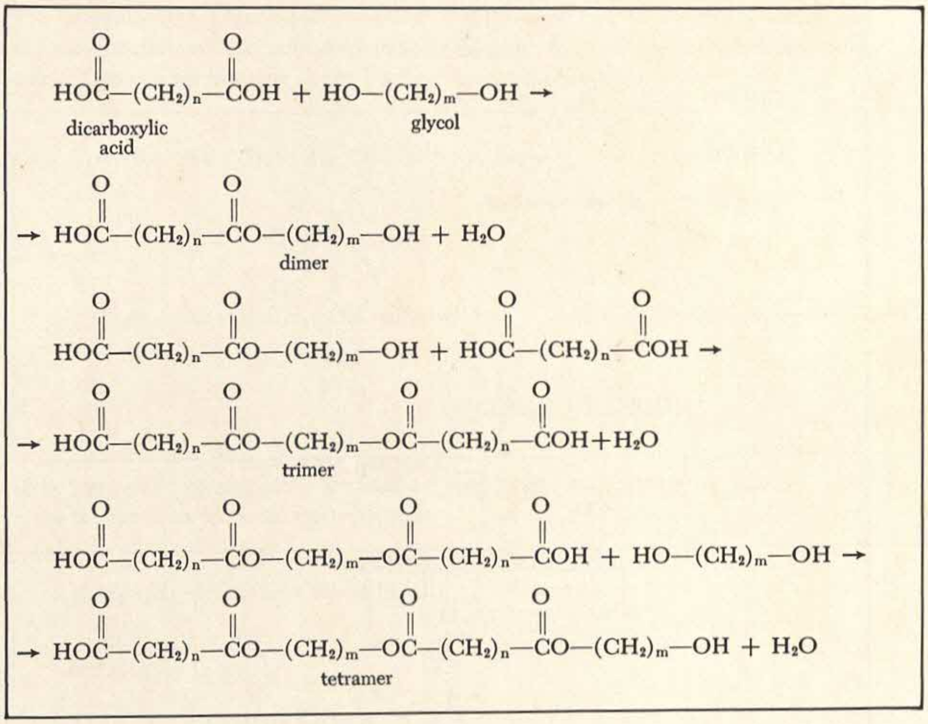
A macromolecular substance—or polymer—is an assembly of molecules, each one formed by the union of a large number of simple molecules (monomers). The aggregate has a high average molecular weight.

Study and research in the last few years have resulted in the creation of a considerable number of new polymers. Progress is such that a suitable polymer has been created for nearly each specific use. Most of the polymers produced are used in the molding of toys, containers, and similar forms. Some are used in specialized industries for the manufacture of components for boats, aircraft, and automobiles. Other polymers have the property of resisting the attacks of aggressive chemical agents; these are employed as essential parts of chemical plants and equipment. Some polymers are transparent and are replacements for glass; others are used in the manufacture of artificial and synthetic textiles and leathers.

Polymers can be divided into two large categories, according to the reaction leading to their formation. These classes are condensation polymers and addition polymers.

CONDENSATION POLYMERS

In general, any molecule having at least two reactive groups is capable of giving rise to the formation of polymers. The reaction mechanism (known as polycondensation) is analogous to any condensation reaction between the reactive groups of two different molecules. These reactive groups unite and eliminate water—or some other substance—as a secondary product. If two different molecules are to produce polycondensation (for a compound with a high molecular weight), both of them must have at least two reactive groups. For example, a dicarboxylic acid can react with a glycol to form a polyester macromolecule.



$$\begin{aligned}
&\underset{\text{dicarboxylic acid}}{\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}} + \underset{\text{glycol}}{\mathrm{HO}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{OH}} \rightarrow\\
&\rightarrow \underset{\text{dimer}}{\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{OH}} + \mathrm{H_2O}\\
&\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{OH} + \mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} \rightarrow\\
&\rightarrow \underset{\text{trimer}}{\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH}} + \mathrm{H_2O}\\
&\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{OH} + \mathrm{HO}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{OH} \rightarrow\\
&\rightarrow \underset{\text{tetramer}}{\mathrm{HO}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{O}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\text{—}(\mathrm{CH_2})_n\text{—}\overset{\mathrm{O}}{\overset{\|}{\mathrm{C}}}\mathrm{O}\text{—}(\mathrm{CH_2})_m\text{—}\mathrm{OH}} + \mathrm{H_2O}
\end{aligned}$$

The reaction in which the polycondensate is formed proceeds by successive stages. The condensation occurs between the acid reactive group ($-COOH$) and the alcohol reactive group ($-OH$). It is accompanied by the formation of water and leads to the production of a chain. This chain gradually attracts two, three, four, or more molecules to subsequent union and leads to the formation of di-

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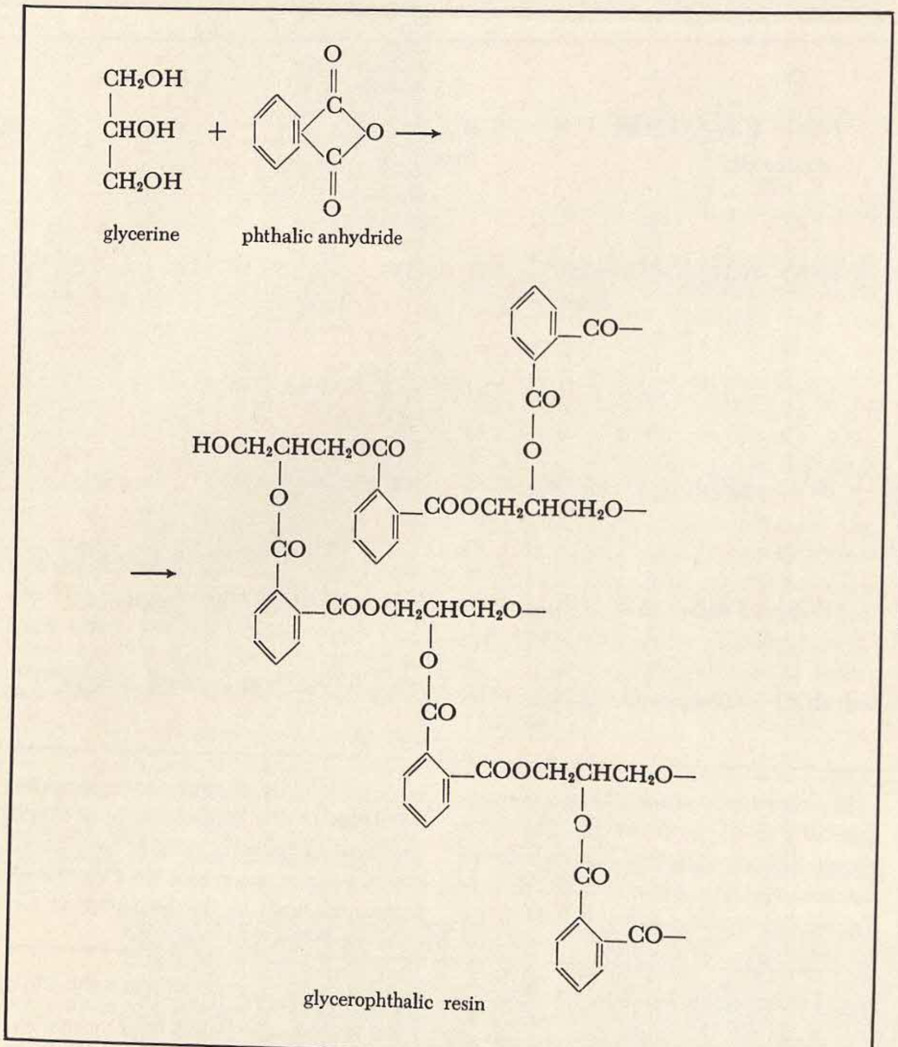
PLANT FOR THE PRODUCTION OF TERITAL®—This illustration shows a portion of an industrial chemical plant for the production of Terital®, which is the commercial name for a polymer employed as a synthetic textile fiber. It is prepared by means of a condensation reaction from terephthalic acid and ethylene glycol. Shown is the section of the plant where the finished product is conditioned, prepared, and shipped. The size of the tanks can be gauged by the height of the man in the lower right corner of the photograph.

1

mers, trimers, tetramers, and so forth. By this process, the molecule grows until it becomes long; consequently, it develops into a molecule of high molecular weight.

In addition to the polymers that develop in a linear manner (such as described above), polycondensation products can have a three-dimensional development. In such a case, at least one of the reacting monomer molecules must have more than two reactive groups.

A polymer with a three-dimensional structure is obtained by means of the polycondensation of phthalic anhydride with glycerine. This process is shown below.



A peculiar characteristic of the polycondensation reaction is that it proceeds by successive stages. The greater part of the reacting mass at each stage is made up of molecules of the same length—molecules of the same degree of polymerization. Each molecule then grows in the same manner during the next stage, by the addition of another monomeric unit. The formation of a polymer is thus a gradual process.

If growth of a polymer is to continue until a technically useful product of high molecular weight is obtained, the reacting monomers must be extremely pure. The presence of impurities always gives rise to secondary reactions that bring the elongation of molecules to a halt.

Polycondensation—like all other condensations—is an equilibrium reaction. Therefore, the secondary product (usually water) is removed so that the desired polymer is the sole product. Moreover, the reaction proceeds faster if the water is removed rapidly. Industrially, this dictates that the secondary product be removed as quickly as it is formed.

ADDITION POLYMERS

The reaction leading to the formation of addition polymers (polyaddition) differs from polycondensation. Polyaddition does not involve the formation of any secondary product. If a molecule is to be able to give rise to the formation of a polymer, it must contain at least one double bond. The polyaddition reaction consists of the union of monomer molecules in place of the double bond, resulting in a

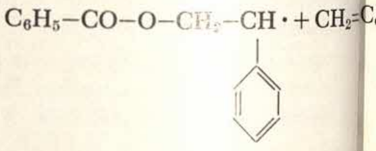
2

a

POLYSTYRENE—The polystyrene resins are obtained by means of the polymerization of styrene, or by the copolymerization of this monomer with other substances, in order to obtain polymers with particular characteristics. The polystyrene resins constitute a group of plastic materials of great importance. They have an appearance similar to that of glass—hard and transparent. They can be readily colored and formed into the desired shape by extrusions or injection molding.

Illustration 2a shows a plant for the production of polystyrene. Illustration 2b shows a product made from polystyrene resins.

polymer whose chain contains no saturated bonds. An example of this kind of



$C_6H_5-CO-O-CH_2-CH\cdot + CH_2=C$

The polyaddition reaction proceeds according to a mechanism involving free radicals. The first stage of the reaction is the formation of free radicals. These are formed by the decomposition of labile molecules, through the effect of heat or

$C_6H_5-CO-O-O-C$

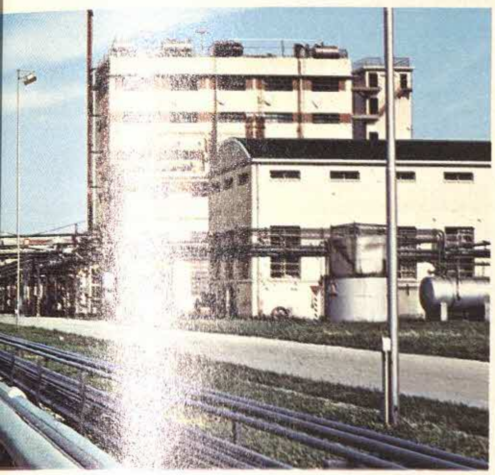
or

$C_6H_5-CO-O-O-C$

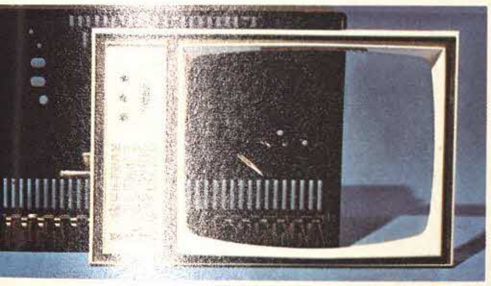
The free radicals formed in this decomposition ($C_6H_5-CO-O-C_6H_5$) give rise to the second stage of polyaddition

$C_6H_5-CO-O\cdot + CH=$

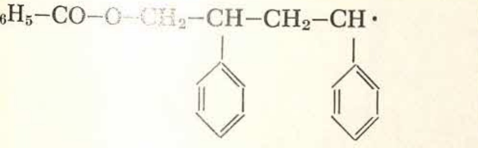
The product of this reaction—once



b



reaction is the formation of polystyrene, represented below.

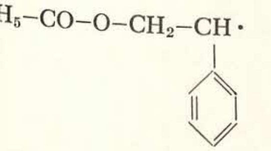


light. The substances giving rise to free radicals are known as initiators and can be of various kinds, although peroxides are generally used. An example is benzoyl peroxide, which decomposes in the following manner:

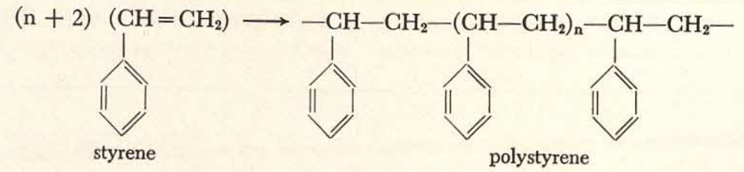
$H_5 \rightarrow 2\,C_6H_5-CO-O\cdot$

$H_5 \rightarrow 2\,C_6H_5\cdot + 2\,CO_2$

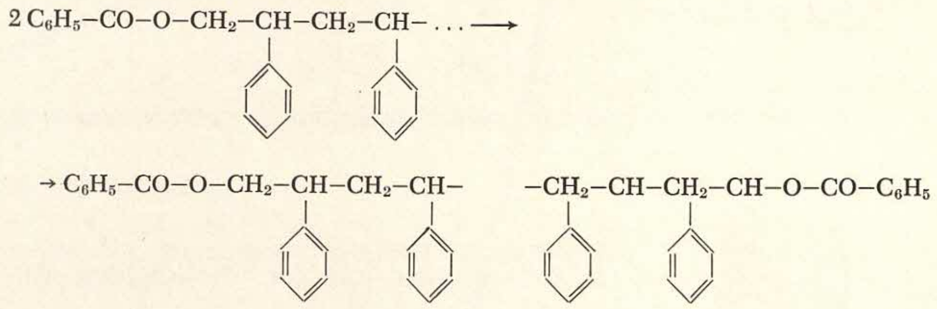
reaction—the growth stage. The free radicals attack the double bond monomer and become attached to it.



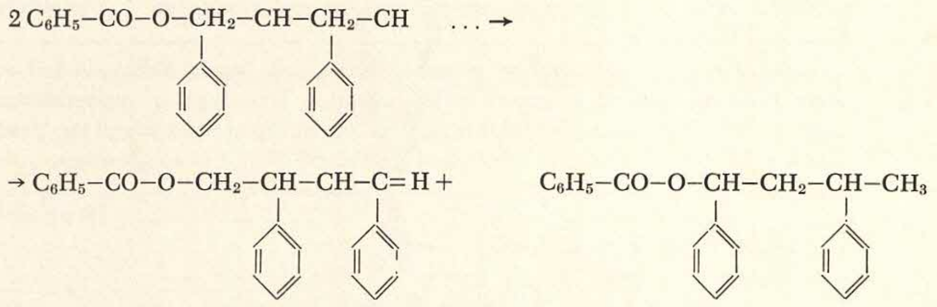
again an active one—attacks the double bond of another styrene molecule, thereby causing the growth of a macromolecular chain, which is represented by the following structure.


$(n+2)\ (CH=CH_2) \longrightarrow -CH-CH_2-(CH-CH_2)_n-CH-CH_2-$
styrene
polystyrene

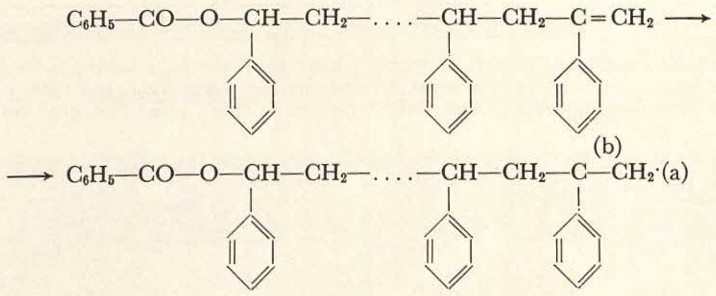
The polyaddition terminates as a result of the deactivation of the activated molecules. This can be brought about by the collision of two free radicals, which are then united by means of a coupling mechanism shown below:


$2\,C_6H_5-CO-O-CH_2-CH-CH_2-CH-\ldots\longrightarrow$
$\rightarrow C_6H_5-CO-O-CH_2-CH-CH_2-CH-$
$-CH_2-CH-CH_2-CH-O-CO-C_6H_5$

or by means of a disproportionate mechanism in which an H• is transferred from one of the radicals to the other.

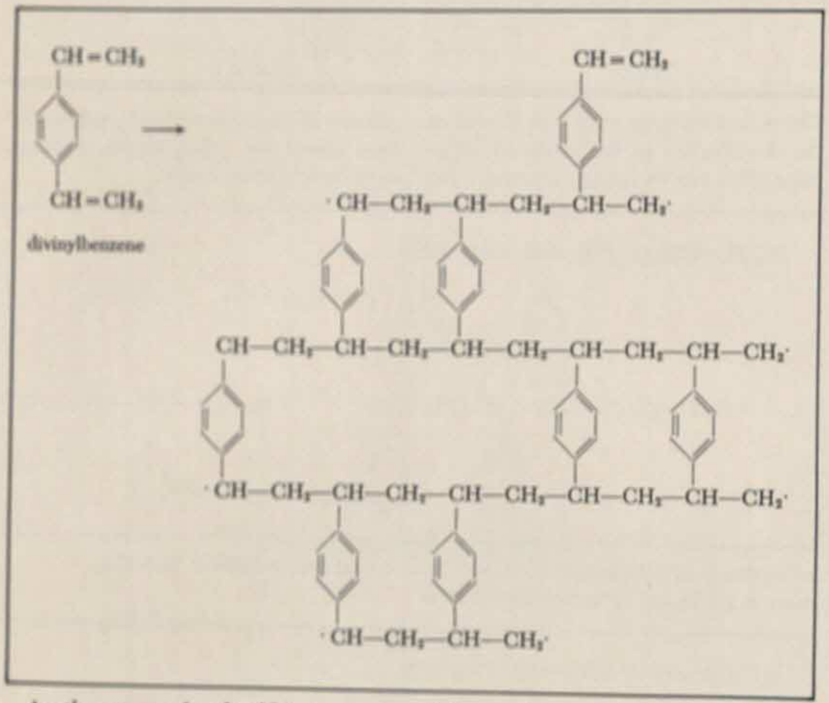

$2\,C_6H_5-CO-O-CH_2-CH-CH_2-CH\ \ldots\rightarrow$
$\rightarrow C_6H_5-CO-O-CH_2-CH-CH-C=H+$
$C_6H_5-CO-O-CH-CH_2-CH-CH_3$

This schematic representation of the deactivation process highlights the formation of double bonds in the mass of the polymer. These double bonds can react further by capturing free radicals, which break them, and attaching themselves at (a) or (b), as shown in the structure below.

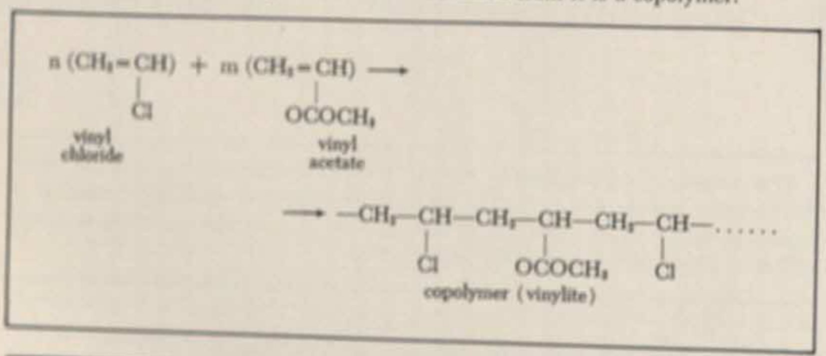

$C_6H_5-CO-O-CH-CH_2-\ldots-CH-CH_2-C=CH_2\longrightarrow$
(b)
$\longrightarrow C_6H_5-CO-O-CH-CH_2-\ldots-CH-CH_2-C-CH_2\cdot$(a)

It is therefore possible for a polymer chain to become lengthened by means of the position bond at (a), and branched by the formation of ramified chain polymers by means of the bond at (b).

Lastly, the deactivation may occur as a result of the interaction of the free radical with a monomer molecule, or a solvent molecule (if one is present). This type of deactivation forms a new free radical for every macromolecule that stops growing; such a radical is capable of inducing polymerization. Also, polyaddition can give rise to polymers with a three-dimensional structure; this happens when the monomer molecule contains at least two double bonds. An example of this is provided by divinylbenzene, which polymerizes in the manner illustrated below.


CH=CH₂
CH=CH₂
divinylbenzene
CH=CH₂
·CH—CH₂—CH—CH₂—CH—CH₂·
CH—CH₂—CH—CH₂—CH—CH₂—CH—CH₂—CH—CH₂·
·CH—CH₂—CH—CH₂—CH—CH₂—CH—CH₂—CH—CH₂·
·CH—CH₂—CH—CH₂·

Another type of polyaddition occurs when different kinds of monomer molecules are mixed. An example of this is the mixture of two differently substituted olefins—such as vinyl chloride and vinyl acetate. This type of polyaddition is called copolymerization and the product obtained from it is a copolymer.



$$n\,(\underset{\underset{\text{Cl}}{|}}{\text{CH}_2=\text{CH}}) + m\,(\underset{\underset{\text{OCOCH}_3}{|}}{\text{CH}_2=\text{CH}}) \longrightarrow$$

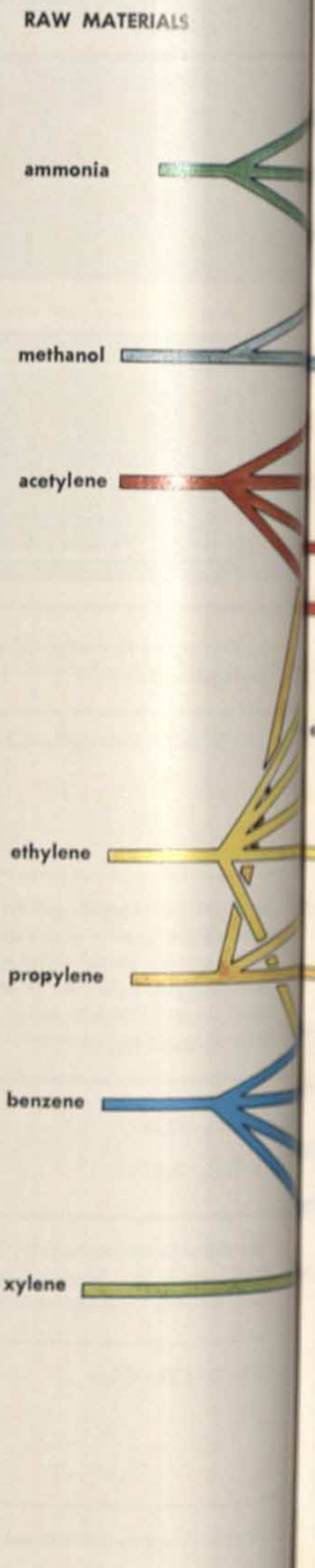
vinyl chloride   vinyl acetate

$$\longrightarrow -\text{CH}_2-\underset{\underset{\text{Cl}}{|}}{\text{CH}}-\text{CH}_2-\underset{\underset{\text{OCOCH}_3}{|}}{\text{CH}}-\text{CH}_2-\underset{\underset{\text{Cl}}{|}}{\text{CH}}-\ldots\ldots$$

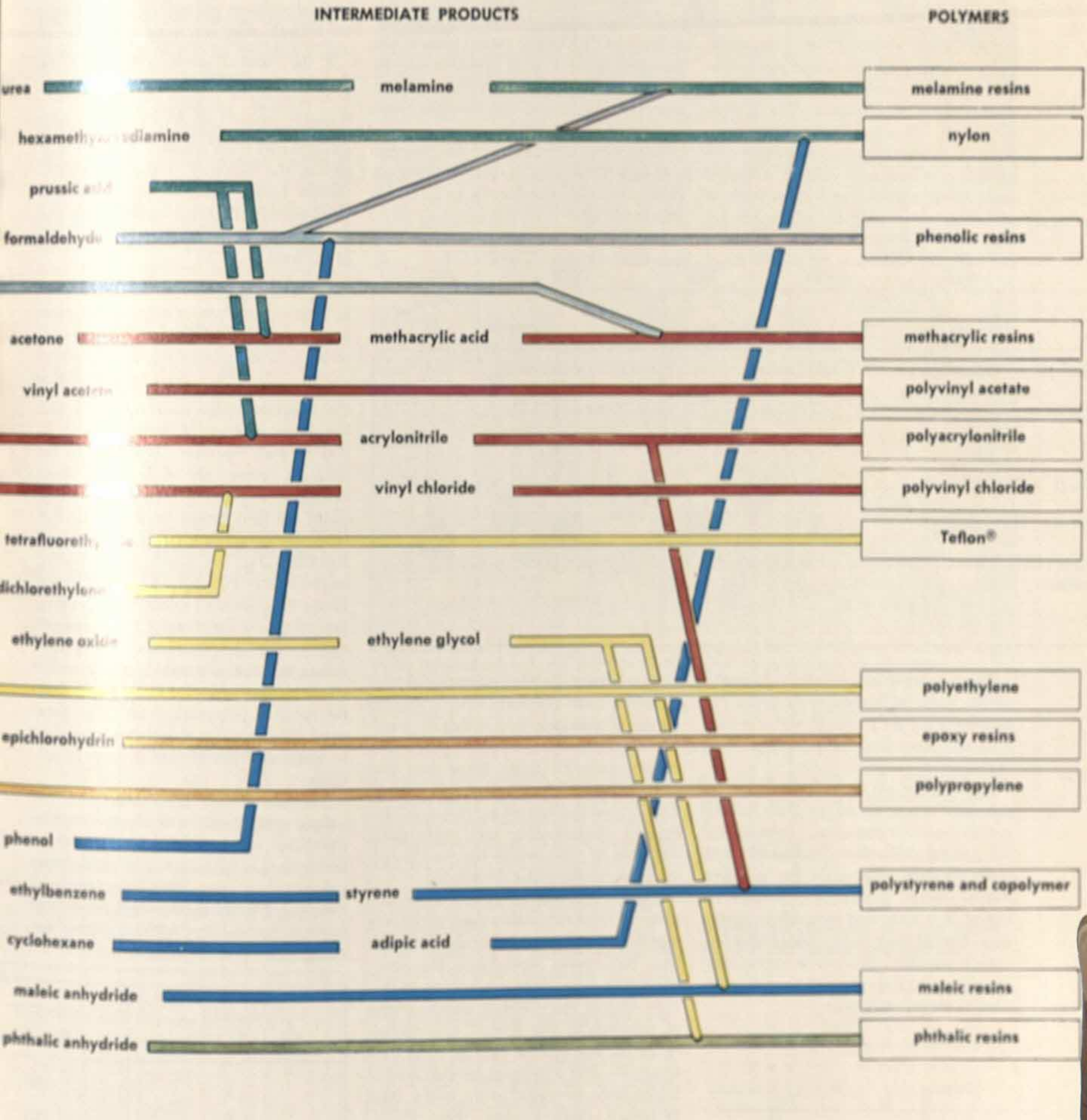
copolymer (vinylite)

POLYMETHYLMETHACRYLATE—This polymer is one of the most important acrylic resins. It is known commercially as Vedril® and Plexiglas®, both used as a substitute for glass. It is colorless, transparent, and light. Here the polymer is being drawn into long threads.

The polymers—whether they are condensation or addition polymers—are not uniform, but are mixtures of molecules having chains. The lengths of these chains vary within a certain range—that



of macromolecules belonging to the same homologous series. The physicochemical characteristics of the polymers are determined not only by the nature of the monomer (or monomers) from which they are derived, but also by the structure of the macromolecule that is formed. Polymers with a linear structure are thermoplastic (softening as the temperature increases); polymers with a three-dimensional structure are thermosetting (assuming an increasingly solid structure until they become hard and can no longer be molded).



PHYSICAL CHEMISTRY OF POLYMERS

the effects of macromolecular structure

Many diverse materials actually have similar physical, chemical, and structural properties. Included in these are important industrial products such as rubber, paints, fibers, and plastics. The feature all have in common is that they are composed of macromolecules—molecules with enormous dimensions when compared with common molecules such as those of water or acetone. These substances are also called polymers, because they consist of many relatively simple chemical units called structural units. A polymer is, therefore, identified on the basis of the chemical formula of its structural unit, and by an index *n*, which indicates the number of times that this structural unit appears in the molecule.

The molecules from which the polymer is obtained are called monomers, because each molecule corresponds to a single structural unit.

Some of the more common polymers are listed below.

Polymer	Structural unit	Monomer
polyethylene $(CH_2-CH_2)_n$	$-CH_2-CH_2$	ethylene $CH_2=CH_2$
polystyrene $(\underset{C_6H_5}{\underset{\mid}{CH}}-CH_2)_n$	$-\underset{C_6H_5}{\underset{\mid}{CH}}-CH_2-$	styrene $\underset{C_6H_5}{\underset{\mid}{CH}}=CH_2$
nylon 6 $(\underset{H}{\underset{\mid}{N}}-(CH_2)_5-\underset{O}{\underset{\|}{C}})_n$	$-\underset{H}{\underset{\mid}{N}}-(CH_2)_5-\underset{O}{\underset{\|}{C}}-$	caprolactan $H-\underset{H}{\underset{\mid}{N}}-(CH_2)_5-\underset{O}{\underset{\|}{C}}-OH$
natural rubbers $(CH_2-CH=\underset{CH_3}{\underset{\mid}{C}}-CH_2)_n$	$-CH_2CH=\underset{CH_3}{\underset{\mid}{C}}-CH_2-$	isoprene $CH_2=CH-\underset{CH_3}{\underset{\mid}{C}}=CH_2$

The *n* index of commercial polymers is of the order of several thousands. The molecular weight is consequently several thousand times that of the corresponding monomer.

Applications of the various types of polymers relate to all of their several properties—their chemical, physical, and mechanical behavior. Compared with more traditional materials, the polymers display special properties that have resulted in a wide and expanding usefulness. One of their most outstanding features is elasticity. This can be appreciated by comparing the values of Young's modulus in various materials:

Material	$E \times 10^{-10}$ (dyne/cm^2)
steel	220
glass	70
polystyrene	3.4
nylon	2
polyethylene	0.24
rubber	0.002

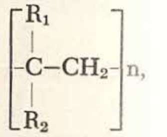
In addition to the characteristic of elasticity, most polymers have a specific gravity (mass per unit volume) varying between one and two grams per cubic centimeter—much lower than that of materials such as glass and metals. This makes the use of polymers advantageous economically and particularly desirable in cases where the weight factor is of fundamental importance.

The low thermal and electrical conductivity of polymers makes them extremely useful as insulating materials, although they have some undesirable characteristics that limit their application in this area. One of the principal disadvantages of polymers is the limited temperature range in which they can be employed. Generally, the maximum temperature at which they are useful—even in the most favorable cases—is less than 250° C (482° F).

The macroscopic properties of polymers depend on a combination of different factors, including those listed below.

1. the type of structural unit
2. the molecular weight
3. the spatial arrangement of structural units in the molecule
4. the spatial arrangement of the chains in the mass of the polymer (termed "packaging")

The various physical and chemical characteristics are reflected in the behavior of the polymer, resulting in substances having different properties and, consequently, different applications. For example, in the series of vinylic polymers of the form



$$\left[-\underset{R_2}{\underset{\mid}{\overset{R_1}{\overset{\mid}{C}}}}-CH_2-\right]n,$$

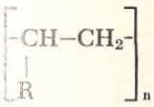
the behavior of the material varies with the chemical nature of the substituents R_1 and R_2 and, therefore, according to the different forces exerted between atoms belonging to different parts of the same chain (or to different chains). This variance can be substantial. If $R_1=CH_3$ and $R_2=COOCH_3$, the result is polymethyl methacrylate (Plexiglas®), well known for its transparency, rigidity at room temperature, and resistance to atmospheric agents. The characteristics of this substance make it a suitable substitute for glass. If, however, $R_1=H$ and $R_2=OH$, the result is polyvinyl alcohol, the principal characteristic of which is solubility in water and insolubility in organic solvents.

The factor that most determines the unique characteristics of a polymer is its molecular weight. As molecular weight increases, the physical and mechanical properties vary from those of a fairly viscous liquid to those of a rigid solid. This is illustrated by the following table for the polymer polyethylene:

Number of structural units	Molecular weight
1	30
6	170
140	4,000
1,400	40,000
14,000	400,000

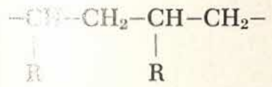
When the molecular weight increases above a certain value, the properties of a polymer remain constant. Because of this, it is particularly important that the product obtained in a process of polymerization have a molecular weight in excess of that certain value. It is also important that, during the reaction leading to formation of a polymer, factors be present that give rise to different values of *n* for the various chains.

The molecular weight of a mass of such molecules is really an average value. It is quite possible for different distributions of *n* to give the same average molecular weight. For the same average molecular weight, the product having the larger percentage of molecules with small *n* value will tend to have inferior properties. Two polymers made up of the same structural unit and having the same molecular weight may differ because of the manner in which the units are united to form the chain. An example is a vinylic polymer of the type



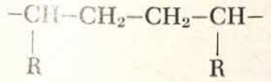
$$\left[-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\right]_n$$

The union of two successive units can occur in such a manner that the terminal part of one unites with the initial part of the other (a head-tail union):



$$-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-$$

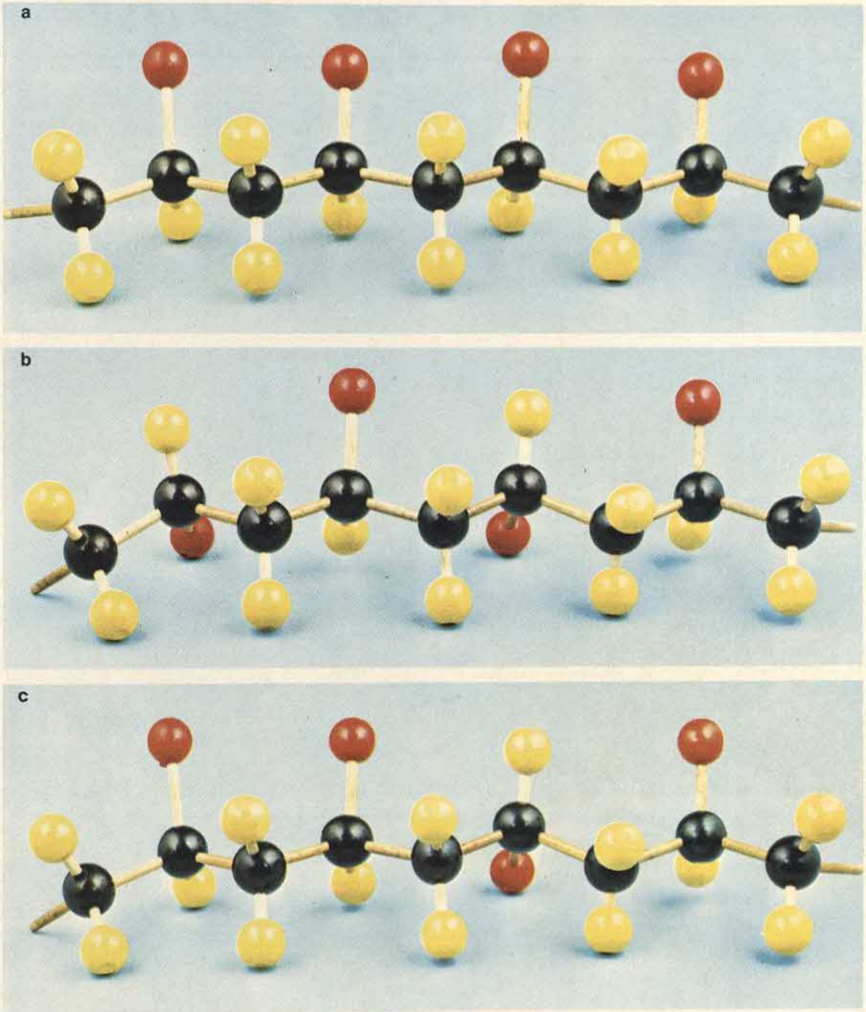
or in such a way that the units are joined by their terminal or initial parts (head-head or tail-tail union):



$$-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-\mathrm{CH_2}-\mathrm{CH_2}-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{CH}}}-$$

In general, the head-head union occurs rarely—compared with the head-tail union—but the presence of a number of these abnormal bonds can lead to variations in the characteristics of the polymer.

1



STEREOREGULAR POLYMERS—In Illustration 1a, an isotactic polymer, the R-groups (indicated as red spheres) are all on the same side of the plane containing the carbon atoms of the molecule.

In Illustration 1b, a syndiotactic polymer, the R-groups are alternately on either side of the plane containing the principal chain.

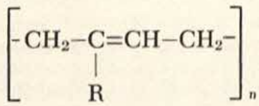
Illustration 1c shows the R-groups oriented in a random manner with respect to the principal chain. Such polymers are atactic.

In addition, the spatial orientation of the R-group with respect to the plane containing the principal chain can differ and give rise to polymers with differing properties—even though they correspond to the same chemical formula. Such polymers are known as stereoisomers, qualified as isotactic, syndiotactic, or atactic, according to the various orientations of the substituents.

Characteristics of the product at room temperature
gas
liquid
wax
hard resin
hard resin

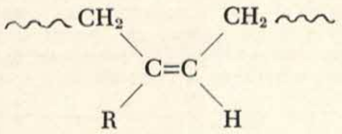
The possibility of crystallization depends on the regularity of the molecular structure. Generally, the atactic polymers do not crystallize and the isotactic polymers have the greatest capacity for crystallization. Because the greater degree of crystallinity corresponds to the greater values of density, hardness, and softening point—as well as to lower solubility—it is important to perfect stereospecific methods of polymerization (methods to obtain products of isotactic or syndiotactic type, rather than atactic products).

Another example of the way the geometry of structural units influences the properties is found in the polydienes

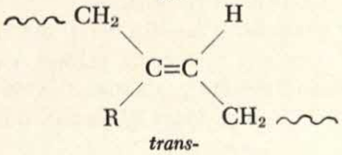


$$\left[-\mathrm{CH_2}-\underset{\displaystyle \mathrm{R}}{\underset{|}{\mathrm{C}}}=\mathrm{CH}-\mathrm{CH_2}-\right]_n$$

in which the structural unit can assume two different spatial configurations

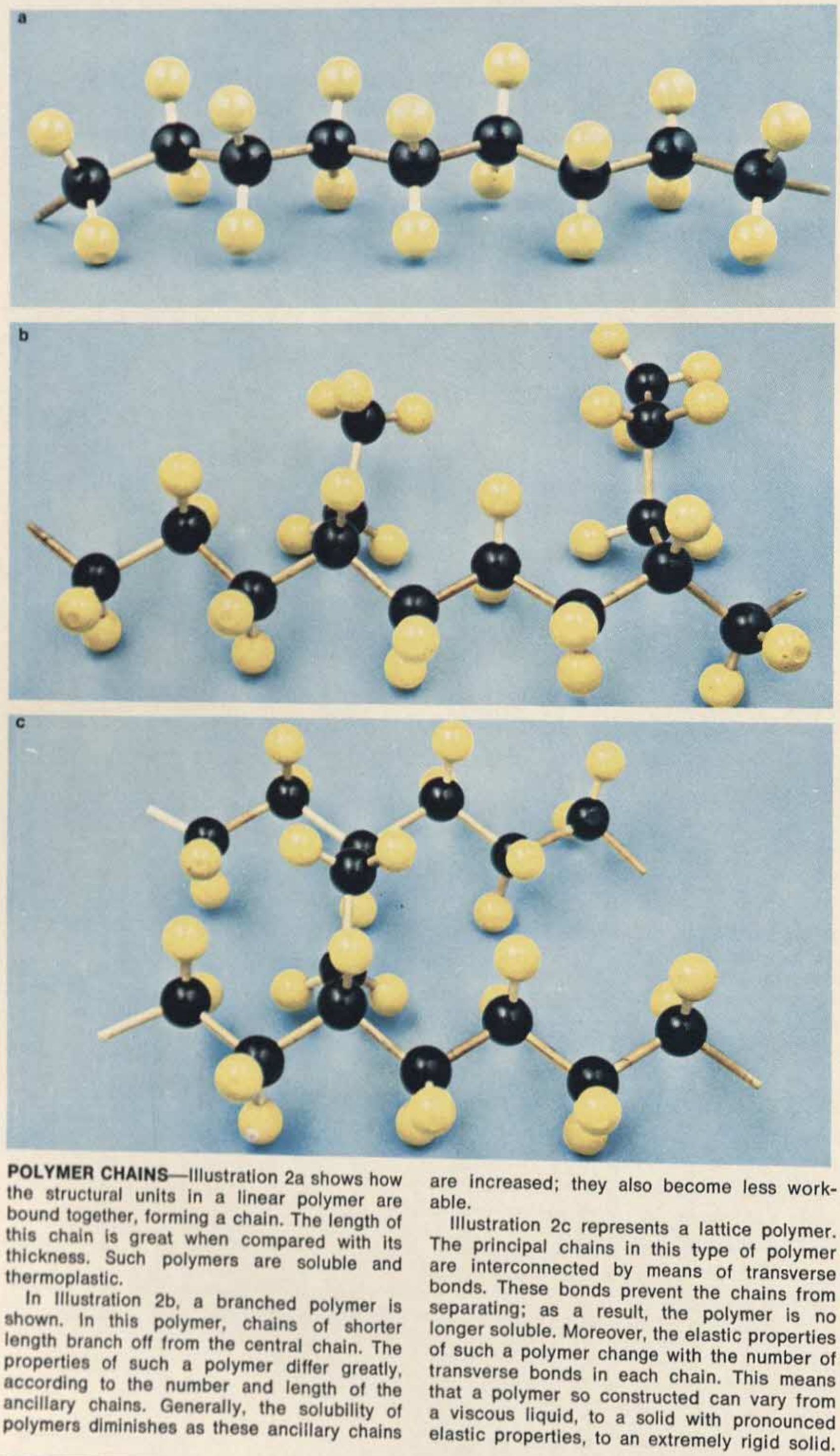


cis-



trans-

to which correspond two products of



POLYMER CHAINS—Illustration 2a shows how the structural units in a linear polymer are bound together, forming a chain. The length of this chain is great when compared with its thickness. Such polymers are soluble and thermoplastic.

In Illustration 2b, a branched polymer is shown. In this polymer, chains of shorter length branch off from the central chain. The properties of such a polymer differ greatly, according to the number and length of the ancillary chains. Generally, the solubility of polymers diminishes as these ancillary chains are increased; they also become less workable.

Illustration 2c represents a lattice polymer. The principal chains in this type of polymer are interconnected by means of transverse bonds. These bonds prevent the chains from separating; as a result, the polymer is no longer soluble. Moreover, the elastic properties of such a polymer change with the number of transverse bonds in each chain. This means that a polymer so constructed can vary from a viscous liquid, to a solid with pronounced elastic properties, to an extremely rigid solid.

quite different characteristics.

For example, when $R = CH_3$, the *cis*-form gives rise to natural rubber, well known for its elastic properties; the *trans*-form, on the other hand, gives rise to the hard, tough substance called gutta-percha.

Differences in geometry are not confined to the structural units; these units also can be grouped in different manners. The various groupings produce linear polymers, branched polymers, or lattice polymers. A polymer always has a large number of chains and the physical state of the product depends on the spatial arrangement of these chains.

In general, the physical state of a compound is determined by the type and the magnitude of the forces (the cohesive forces) exerted between the molecules. These forces can be divided into different types: dispersion forces, inductive forces, and hydrogen bonds.

Every molecule has a particular distribution of electron charge. This charge may be distributed either symmetrically or asymmetrically around the nucleus. When the distribution of the charge in a molecule is not symmetric (as in polar molecules), the center of the distribution of the electron charges does not coincide with the center of the positive charges. Such a molecule has a permanent dipole moment.

The permanent dipole moments can create induced moments in other molecules, altering the electron distribution of these molecules. Moreover, even when the electron distribution is symmetrical, instantaneous dipole moments result from momentary fluctuations of the electron distribution. Interactions between dipoles are of different types: dispersion forces (interactions between instantaneous dipoles); dipole forces (interactions between permanent dipoles); and inductive forces (interactions between dipoles and induced dipoles).

A type of bond stronger than those so far mentioned—although weaker than a true chemical bond—is the so-called hydrogen bond. This can be represented by the general formula A—H . . . B, and can exist between a hydrogen atom covalently bound to a strongly electronegative atom (A) and an electronegative atom (B) not directly bound to the hydrogen atom.

All the forces together determine the distance between the molecules at a given temperature and this distance is responsible for the physical state of the substance.

In polymer chains, the regularity of the arrangement of structural units along the chains can be decisive in ensuring that the forces will be exerted in the desired manner. This arrangement, therefore, has an important influence on the consistency and characteristics of the polymer.

AROMATIC COMPOUNDS | an important starting point in organic chemistry

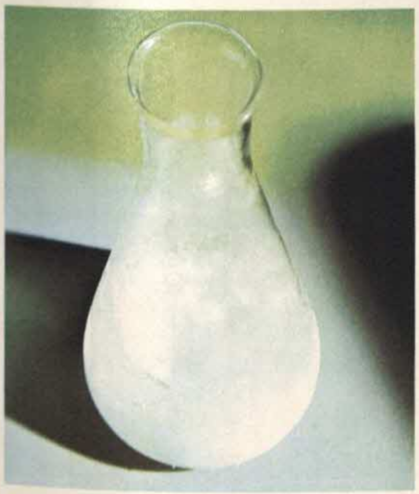
Benzene, an important compound whose molecules are hexagonal ring structures, was discovered by the English physicist and chemist Michael Faraday. Benzene is the basic raw material for a vast range of products. In fact, organic chemistry is much in debt to benzene. Thanks to the chemical properties of the benzene molecule, which render it suitable for a large number of reactions, it constitutes the basis for the entire organic chemistry of aromatics.

PHYSICAL PROPERTIES

Benzene is a colorless liquid that boils at 80.1° C (about 176° F) and crystallizes at 5.4° C (about 42° F). It is highly flammable and burns with a smoky flame, and it has a pleasant aromatic odor. If benzene vapors are inhaled for a long time, however, acute poisoning that produces hemorrhages in various internal organs can occur. Paralysis of the motor centers may occur. Chronic poisoning is also a danger; protracted inhalation of benzene vapor in most cases leads to death. The toxic effect of benzene is a blockage of the medullary activity of the spinal cord and a great reduction in the number of white blood corpuscles (the loss may be as much as 90 to 95 percent). As a result, the organism is deprived of its defenses and is thus vulnerable to all types of infection. Benzene is used extensively in industry; consequently, the most rigorous safety precautions must be applied when it is in use. This is particularly true when benzene is used as a raw material for the production of other products such as styrene, the starting point for synthetic rubber, and polystyrene, phenol, aniline, chlorobenzene, nitrobenzene, and maleic anhydride. These uses are quite apart from benzene's widespread use as a solvent.

BENZENE—Benzene is a colorless liquid, which solidifies when cooled to 5.4° C (41.7°F) and forms a white mass consisting of long, highly fragile needles.

1



2

TAR—Coal tar is a raw material that contains a large number of aromatic compounds, of which benzene is one. Tar is used for many purposes, including the making of cardboard and ropes impermeable to water.

COAL TAR

The principal source of benzene is coal tar, which contains a wide variety of aromatic compounds; more than a hundred different substances have been found in it. The starting material for coal tar is ordinary coal. Destructive distillation of coal at 1,100 to 1,200° C (about 2,012 to 2,192° F) yields a range of products, including coal gas and coal tar.

Coal gas, consisting essentially of methane, ethane, acetylene, and carbon monoxide, is also known as illuminating gas; it was widely used during the nineteenth century as a means of public lighting. Today, coal gas is used almost exclusively for heating.

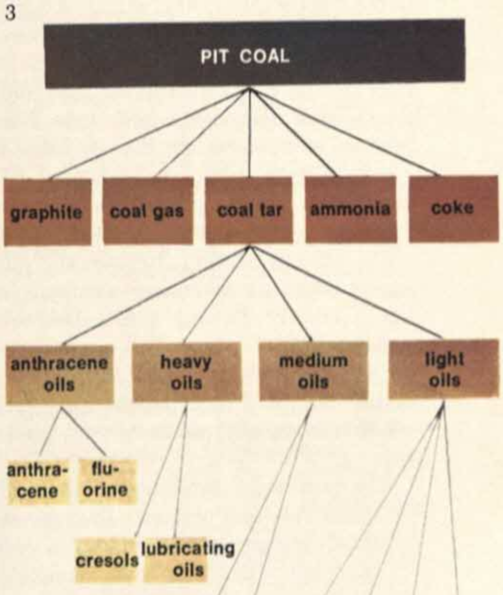
Coal tar in the crude state finds limited application as a means of rendering cardboard, ropes, and wooden stakes impermeable to water. Mixed with pitch and soda it is also used as an industrial disinfectant. Its most important use, however, is as a raw material for many important industrial products. Crude tar obtained from the distillation of coal contains many different substances. A first refining process is, therefore, necessary. This somewhat crude refinement divides the crude tar into portions whose components have more or less similar chemical and physical properties. This process, called fractional distillation, is based on the different boiling points of the various components. The coal tar is boiled and the vapors recondensed; the resulting liquids are thus separated according to their different ranges of boiling points. Four principal fractions are produced:

1. Light oil: liquids collected at temperatures up to 170° C (338° F).
2. Medium oil: liquids collected between 170° and 230° C (338° and 446° F).
3. Heavy oil: liquids collected between 230° and 270° C (446° and 518° F).
4. Anthracene oil: liquids collected up to a temperature of 340° C (644° F).

Light oil is largely benzene, its deriva-

COAL TAR—Coal tar is the principal source of benzene. Among other products derived from coal tar are coal gas, ammonia, and coke. This diagram shows the principal products obtainable from coal.

3



tives (xylene and toluene), and pyridine, a basic nitrogenous compound having a structure similar to the structure of the benzene molecule.

Medium oil consists principally of phenols and naphthalene. Heavy oil contains cresols (derivatives of phenol), higher hydrocarbons such as acenaphthene and diphenyl, and basic products such as quinoline and isoquinoline. The last fraction, anthracene oil, solidifies on cooling and yields a semisolid paste. This substance consists principally of crystallized hydrocarbons containing condensed benzene nuclei, the most abundant of which is anthracene. A solid residue remains in the distillation boiler; this residue is pitch, or asphalt, used as a substitute for natural asphalt in road paving.

These four fractions are collected over fairly wide temperature ranges. Each fraction, therefore, contains several products, as well as impurities that belong to the adjacent higher and lower fractions. A second and more refined separation is, therefore, necessary. The individual fractions are distilled separately to produce technically pure products. This article treats the first fraction—light oil—which contains benzene, toluene, the xylenes, pyridine, and phenol (an impurity from the second fraction).

Pyridine and phenol, with pyridine basic and phenol acidic, are eliminated in the form of salts. They, of course, form salts when they are treated respectively with an acid and a base. The light oil is thus treated first with sulfuric acid and then with a solution of caustic soda. The pyridine and phenol salts that are formed are soluble in water and can thus be eliminated.

Subsequent separation, therefore, takes place between benzene, toluene, and the xylenes. Because these three compounds have different boiling points—benzene boils at 80.1° C (about 176° F), toluene at 110° C (230° F), and the xylenes around 140° C (284° F)—fractional distillation eventually produces pure products.

The number of distillations is reduced in actual industrial practice. The process is based on the use of rectification columns, which permit a more complete separation of the mixture.

SUBSTITUTION REACTIONS OF BENZENE

As previously mentioned, one of the properties of benzene is its considerable resistance to addition reactions. The explanation of this phenomenon lies in resonance theory. Benzene is a compound whose carbon-to-carbon bonds are intermediate between the double bond and the single bond. From the point of view of energy, these bonds are more stable than conjugate double bonds. Despite its reluctance to enter into addition reactions, however, benzene lends itself readily to substitution reactions. In substitution reactions, one or more of the hydrogen atoms of the ring are replaced by monovalent atoms or radicals. The most important substitution reactions are the Friedel-Crafts synthesis, nitration, halogenation, and sulfonation.

TOLUENE—This derivative of benzene contains a methyl group that has replaced a hydrogen atom. Its name is derived from Tolu balsam, the substance from which it was first extracted. Toluene is an important raw material for the production of dyes and explosives (for example, trinitrotoluene, or TNT).

4

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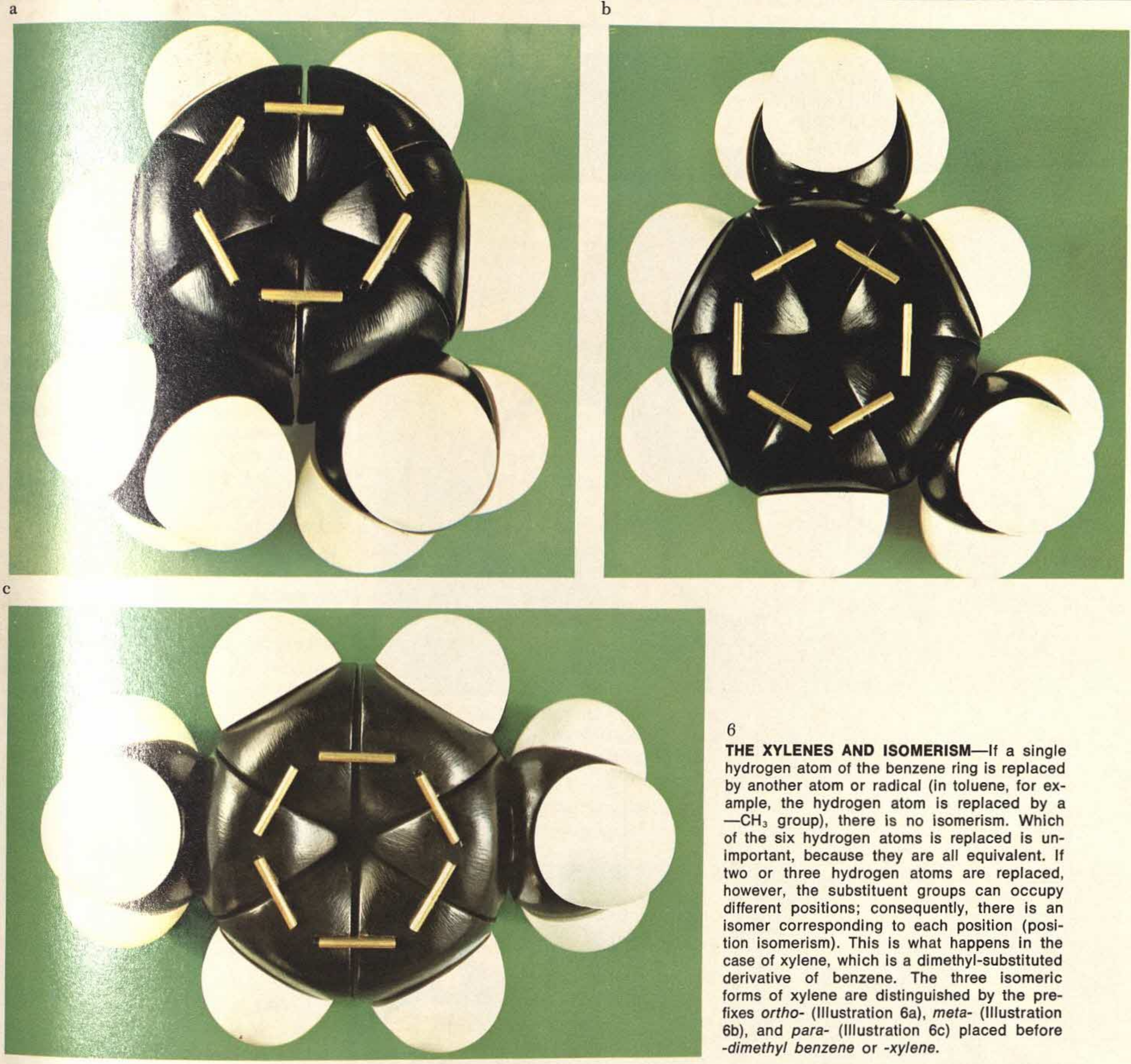
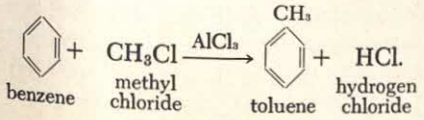
TOLUENE DYES—The dyes derived from toluene include alizarin violet 3B, alizarin green G, alizarin blue 2B, and somalia yellow.



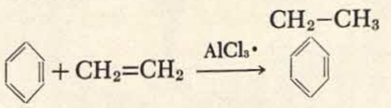
6
THE XYLENES AND ISOMERISM—If a single hydrogen atom of the benzene ring is replaced by another atom or radical (in toluene, for example, the hydrogen atom is replaced by a —CH_3 group), there is no isomerism. Which of the six hydrogen atoms is replaced is unimportant, because they are all equivalent. If two or three hydrogen atoms are replaced, however, the substituent groups can occupy different positions; consequently, there is an isomer corresponding to each position (position isomerism). This is what happens in the case of xylene, which is a dimethyl-substituted derivative of benzene. The three isomeric forms of xylene are distinguished by the prefixes *ortho-* (Illustration 6a), *meta-* (Illustration 6b), and *para-* (Illustration 6c) placed before *-dimethyl benzene* or *-xylene.*

THE FRIEDEL-CRAFTS SYNTHESIS

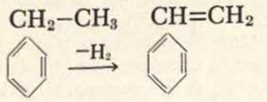
This reaction permits substitution of a large number of hydrocarbon radicals into the benzene ring. It consists of reaction with halogen derivatives of aliphatic hydrocarbons in the presence of aluminum chloride. The aluminum chloride acts as a catalyst:



This synthesis, suitably modified for industrial purposes, is used for the production of styrene, an important intermediate in the production of polystyrene polymers. Ethyl benzene is synthesized by condensing ethylene and benzene in the presence of aluminum chloride.

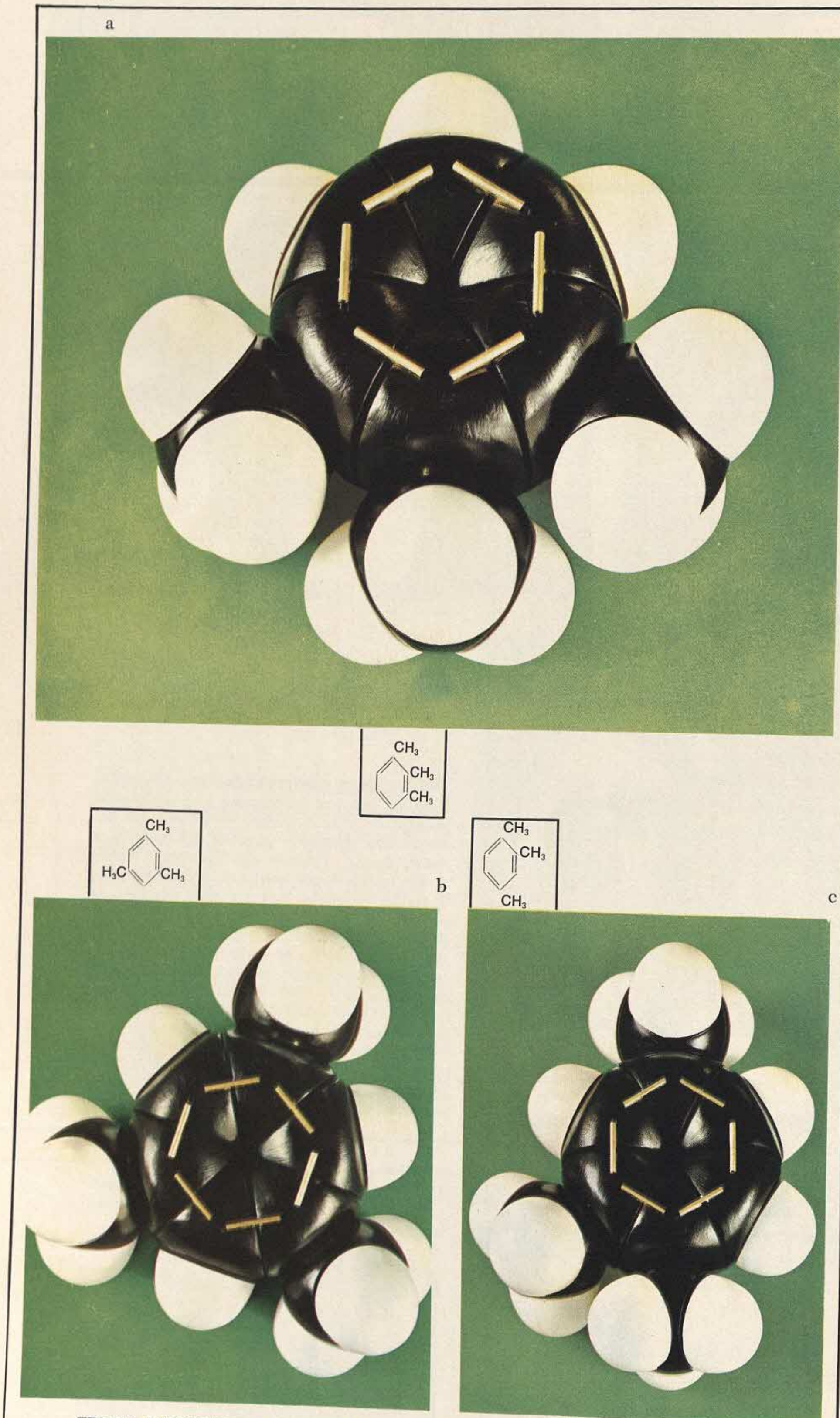


The ethyl benzene is then dehydrogenated, producing styrene:



Other catalysts may also be used. At times these are even more effective than

XYLENE SOLVENTS—This photograph shows a large furrow that has been produced in an organic compound by a xylene solvent.
7



TRIPLY SUBSTITUTED PRODUCTS—The triply substituted benzene derivative also has three possible isomers: together, symmetric, and asymmetric. The tri- and tetra-substituted derivatives, assuming that the substituent groups are identical, have three isomers. In the case of compounds that are penta- or hexa-substituted, however, no possibility of isomerism exists.

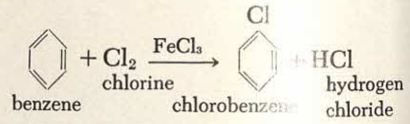
Separation of the three isomers shown here is difficult because of the closeness of the boiling points and requires special techniques. For industrial purposes, use of a mixture of all three isomers is common. Compounds such as these are used in the production of lacquers and paint thinners.

the aluminum chloride. Boron trifluoride, BF_3, and sulfuric acid are two such catalysts.

HALOGENATION

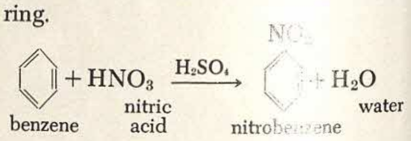
This reaction permits introduction of chlorine and bromine directly into the benzene ring. Iodine and fluorine can also be introduced, but only by indirect methods.

The reaction occurs quite readily at low temperatures in the presence of a halogen carrier—iron(III) chloride, for example—which acts as a catalyst and increases the reaction rate.



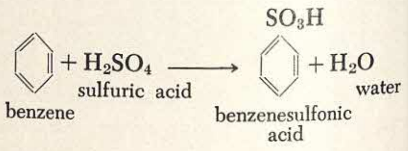
NITRATION

This reaction introduces the $-NO_2$ group. A mixture of nitric acid and sulfuric acid is used. The sulfuric acid supplies a proton and then removes a molecule of water from the species to produce a new, extremely reactive species: the nitronium ion, $+NO_2$, which attacks the benzene ring.



SULFONATION

In this reaction the $-SO_3H$ group is introduced into the benzene ring. The substitution is carried out by reacting concentrated sulfuric acid with benzene. For example,



The sulfonation of benzene is best carried out at a temperature of 170 to 180° C (338 to 356° F). This removes the water produced in the reaction by evaporation. Benzenesulfonic acid, chlorobenzene, and nitrobenzene are important industrial chemicals, because a wide range of organic products is derived from them.

CYCLIC COMPOUNDS

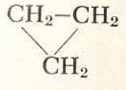
carbon's closed chains

Most hydrocarbons—organic compounds of carbon and hydrogen—have an open-chain structure. These substances are called aliphatic hydrocarbons because many members of the group have an oily consistency. Aliphatic hydrocarbons may be saturated, containing only single bonds (the paraffins, or alkanes), or unsaturated, containing double bonds (the olefins, or alkene hydrocarbons), or triple bonds (the alkyne hydrocarbons).

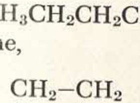
In many hydrocarbons the carbon-atom chain is cyclic, in a closed-chain or ring form. Compounds of this type are said to be cyclic. Cyclic compounds are divided into two groups: aromatic hydrocarbons—the derivatives of benzene; and compounds whose chemical behavior is analogous to the chemical behavior of aliphatic compounds. Such cyclic compounds are called alicylic. These, too, may be either saturated or unsaturated.

$$\text{Hydrocarbons}\begin{cases}\text{open-chain}\\ \text{closed-chain}\begin{cases}\text{alicyclic}\\ \text{aromatic}\end{cases}\end{cases}$$

The number of carbon atoms forming a closed chain cannot be less than three and is sometimes more than 30. The name of such a compound consists of the corresponding aliphatic compound, preceded by the prefix "cyclo-;" thus, there exist cycloparaffins, cycloalkenes, and so forth. For example, propane, $CH_3CH_2CH_3$, corresponds to cyclopropane,



and butane, $CH_3CH_2CH_2CH_3$, is matched by cyclobutane,



In a molecule of the methane type, the four hydrogen atoms bonded to the carbon atom arrange themselves in space in a symmetrical manner. In methane, CH_4, the carbon atom is at the center of a regular tetrahedron; the four bonds are directed toward the vertices of the tetrahedron. Any two of these bonds form an angle of about 109°. This is also the configuration of each carbon atom in the open chains of the paraffins. These chains thus assume an undulating aspect. Put another way, the carbon atoms "zigzag."

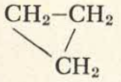
The cyclopropane molecule tends also to take on the most symmetrical arrangement possible; that is, an equilateral triangle with an internal angle of 60°. In a system of this type the bond angle is deformed. As the German chemist Adolf von Baeyer noted in 1885, this deformity produces a strong internal tension that makes the molecule rather unstable. As the number of carbon atoms in the cyclic chain increases, however, the internal tension diminishes. In cyclobutane, for example, the four carbon atoms are located at the corners of a square, and the bond angle is 90°. Thus, cyclobutane should be more stable than cyclopropane. Experience confirms this notion. In cyclopentane and cyclohexane the bond angles are 108° and 120°. These values are very close to those of the tetrahedral arrangement. Thus, these compounds are quite stable.

It might be thought that in closed chains with a greater number of carbon atoms, the bond angles would be greater than 109° (in cyclodecane, for example, the angles should be 144°). The internal tension in large closed chains should, therefore, make this type of molecule impossible. This theory, apparently so plausible, was proved to be untenable by the discovery by the Croatian-Swiss chemist Ruzicka of cyclic compounds with large numbers of carbon atoms in the rings.

A perfume manufacturer had commissioned Ruzicka to identify the structures of musk and civet, two rare and quite costly odorous substances. Musk is produced by a gland in the abdomen of the male musk deer. This animal, similar to the roebuck but without horns, lives mainly in the mountains of Central Asia, especially in the Himalayan region. An adult animal yields 30 to 40 g of musk, which usually contains less than one percent essence of musk. Similarly, civet is obtained from the civet cat, a mammal that resembles the felines and the martens. It lives in Africa, and emanates such a strong odor that it keeps other animals at a distance. Ruzicka discovered that the musk molecule has a closed chain of 15 carbon atoms, and that the civet molecule consists of a closed chain of 17 carbon atoms.

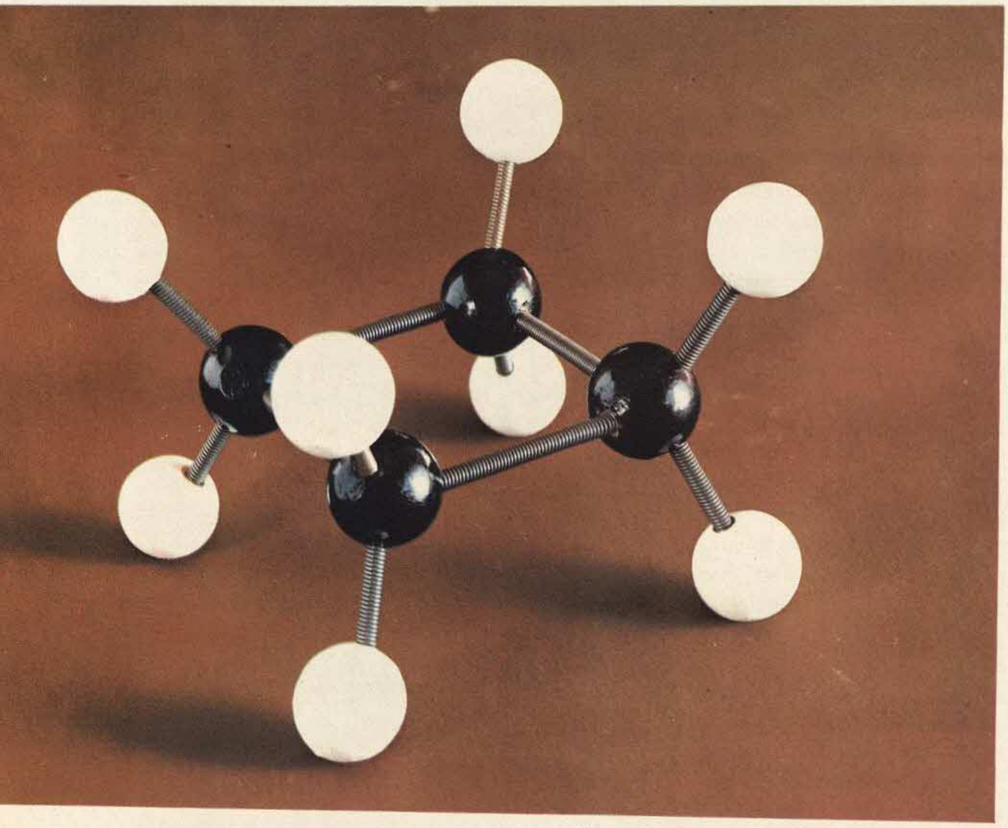
Ruzicka was also able to synthesize alicyclic compounds with closed chains of as many as 44 carbon atoms and a stability equal to that of the paraffins. The theory of internal tension was upset by these facts, and had to be corrected. The carbon atoms of large cyclic molecules have an undulating arrangement just as in the open chains of paraffin hydrocarbons. This eliminates bond-angle tension and permits all the bond angles to remain at about 109°—the optimal value.

The simplest of the alicyclic compounds is cyclopropane:



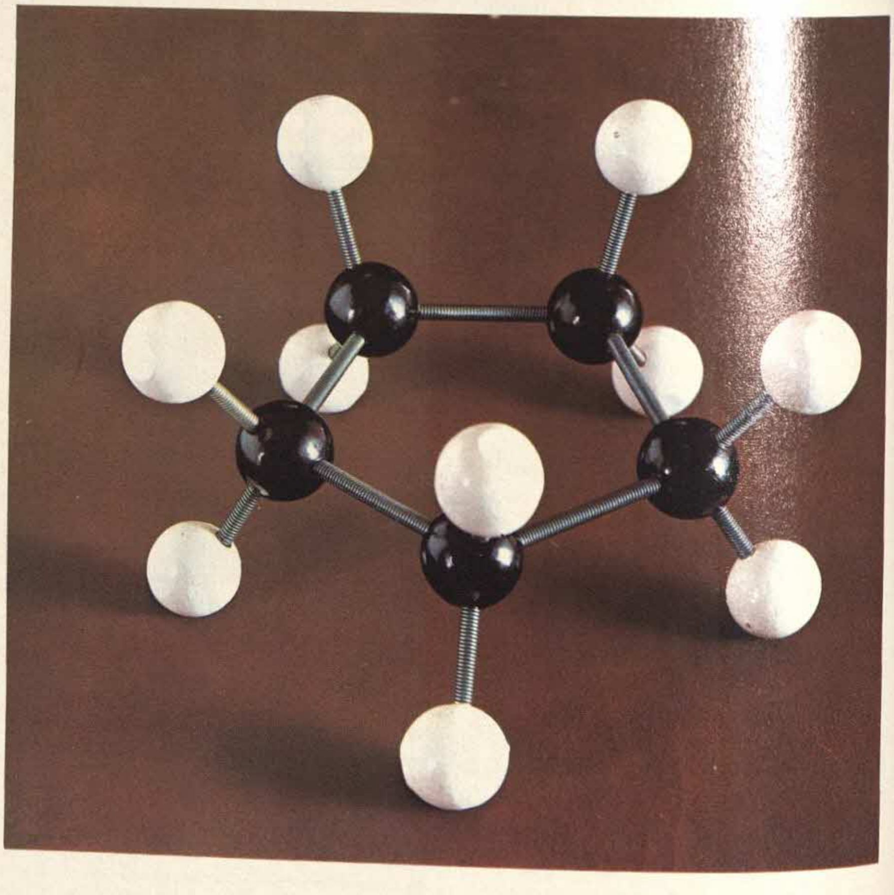
a rather unstable gas that is converted into an isomer, propylene, $CH_3{-}CH{=}CH_2$, by heating. Some of its properties resemble those of propylene, introducing the curious and rare phenomenon of a saturated substance that behaves like an unsaturated substance. Despite its relative instability, the cyclopropane group appears in the molecule of some natural compounds—for example, in the pyrethrins, poisonous substances used as insecticides. These substances have a great advantage over DDT in that they do not cause insects to build up a tolerance; therefore, the pyrethrins retain their effect. Together with similar synthetic products, they are especially useful in agriculture, although it should be pointed out that all synthetic pesticides are now under sharp attack for their potential harm to the environment.

The next member of the group is the 4-carbon-atom molecule cyclobutane, which is less reactive than cyclopropane, at least in ionic reactions. The cyclobutane ring can be opened only under conditions of great energy; that is, at high temperature and pressure and in the presence of suitable catalysts. The closed chain of cyclobutane appears in some natural sub-



CYCLOBUTANE — The 4-carbon-atom ring is less reactive in ionic reactions than the 3-carbon-atom ring. The 4-carbon-atom ring is present in natural substances such as truxilline, which occurs in coca leaves together with the alkaloids of the cocaine group.

2



CYCLOPENTANE—The 5-carbon-atom ring of cyclopentane is quite stable. This hydrocarbon is present in abundance in petroleum crudes. The molecular structures of many natural substances, such as hormones and vitamins, contain a ring similar to it.

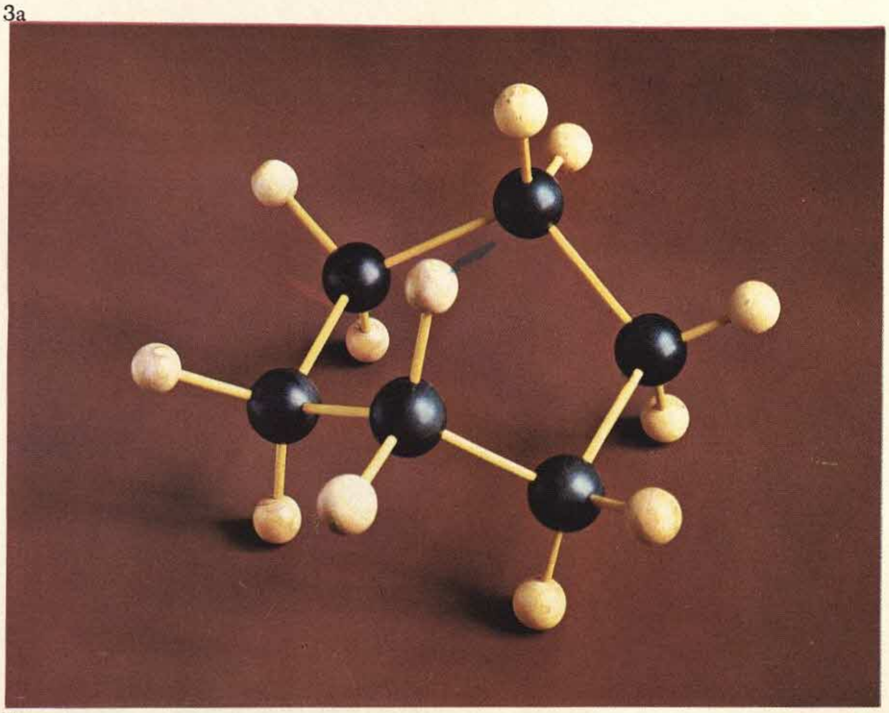
stances, such as truxilline, which occurs in coca leaves together with the alkaloids of the cocaine group.

The 5-carbon-atom ring of cyclopentane is very stable. Cyclopentane is present in abundance in petroleum crudes from several different sources. The molecular skeleton of cyclopentane appears often in nature. Most importantly, it is condensed with other cyclic systems in the basic structure of steroids, a group that includes such substances of biological importance as sex hormones, bile acids, cholesterol, cardiac stimulants, and vitamin D. An isolated ring of 5 atoms is present in the pyrethrins, in jasmine, and also in certain acids extracted from the oil of seeds of various exotic plants.

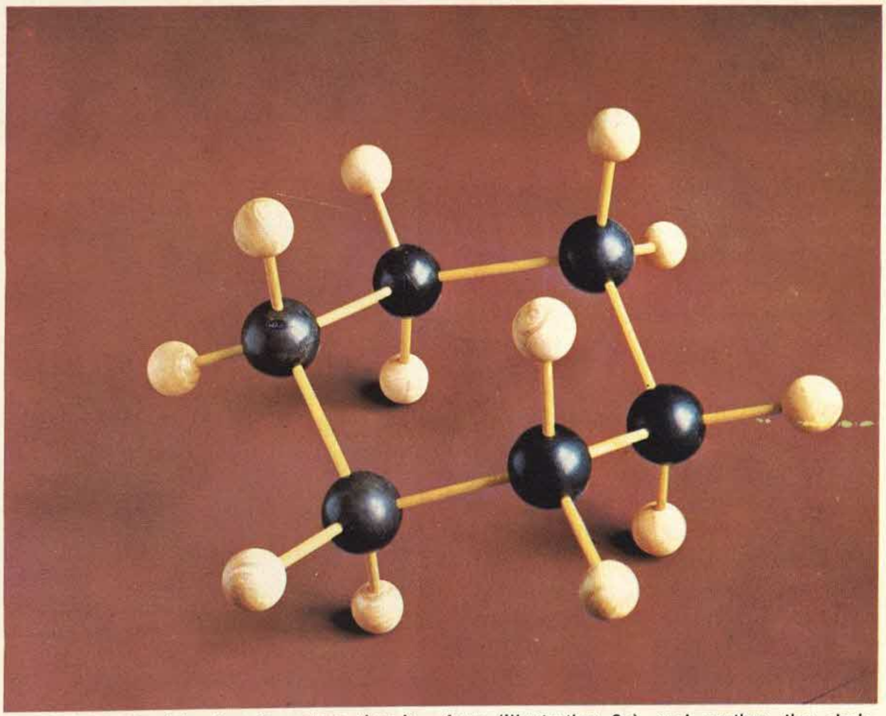
The most important alicyclic compound, both theoretically and in practical application, is undoubtedly cyclohexane. Its derivatives are widespread in nature. For example, it is present in steroids and in terpenes, a vast group that includes such substances as camphor and the fragrances of many flowers. High percentages of cyclohexane and some of its derivatives are also found in petroleum crudes.

The spatial structure of the cyclohexane molecule is most unusual. In 1890 the hypothesis was advanced that the carbon atoms in cyclohexane do not lie on a plane, as von Baeyer had supposed, but rather that they have a zigzag configuration, free of bond-angle strain. Two different spatial models of cyclohexane may be constructed, each of which conserves the normal bond angles. The two configurations are the so-called boat or tub form and the so-called chair form. This hypothesis was discarded at first, for scientists succeeded in producing cyclohexane in one form only. Some 30 years later the idea was revived and demonstrations with models showed that it was possible to change one form to the other by rotation around the single bonds. This rotation produces only a slight distortion of the normal bond angles, and requires a small amount of energy. Thus, the rotation can take place at ordinary temperatures. Moreover, if one of the two forms of cyclohexane could be prepared in the pure state, it would rapidly transform into a mixture of the chair form and the boat form. This mixture makes up common cyclohexane.

3a



3b



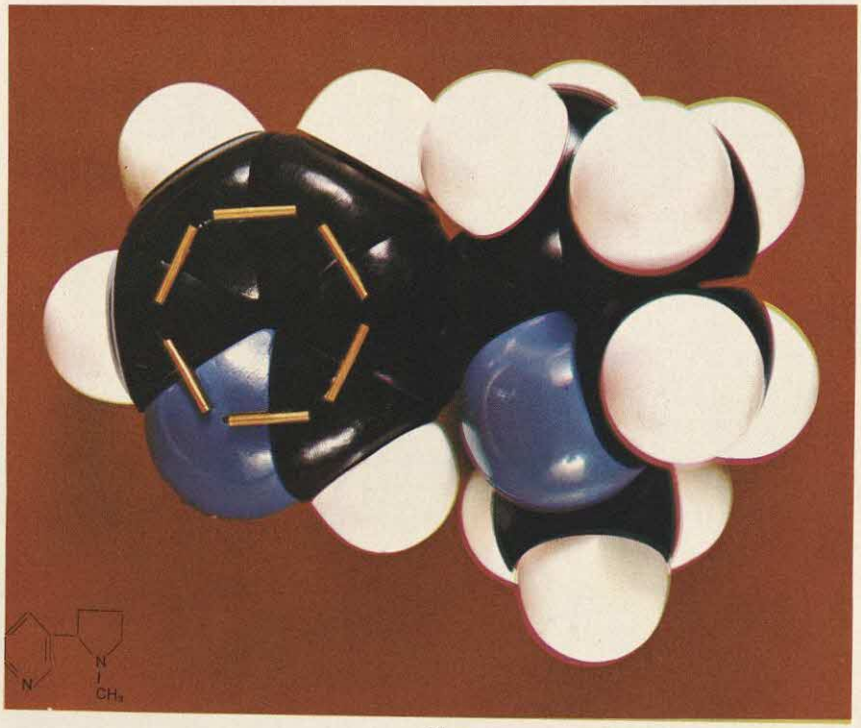
CYCLOHEXANE — The 6-carbon-atom ring is the most stable of all. Its atoms are not all on the same plane, but rather are arranged according to two configurations: one, the boat form (Illustration 3a), and another, the chair form (Illustration 3b). One form converts to the other by means of a simple rotation around the bonds.

Derivatives of cyclohexane are of great importance industrially. They serve as raw materials in the manufacture of the well-known synthetic fiber nylon, for example. Nylon is particularly useful when durability, crush resistance, abrasion resistance, and lightweight strength are of importance.

THE HETEROCYCLIC COMPOUNDS

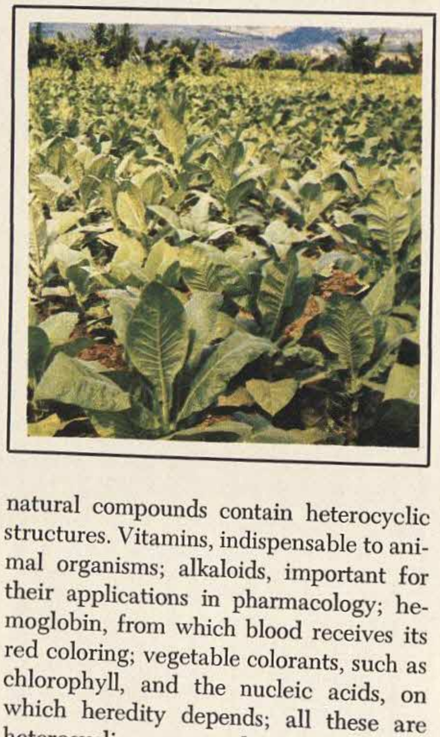
the outsider in the world of carbon

1a



NICOTINE—Many natural substances contain heterocyclic compounds. Tobacco leaves (Illustration 1b) contain nicotine. The molecular structure of nicotine is shown in Illustration 1a.

1b



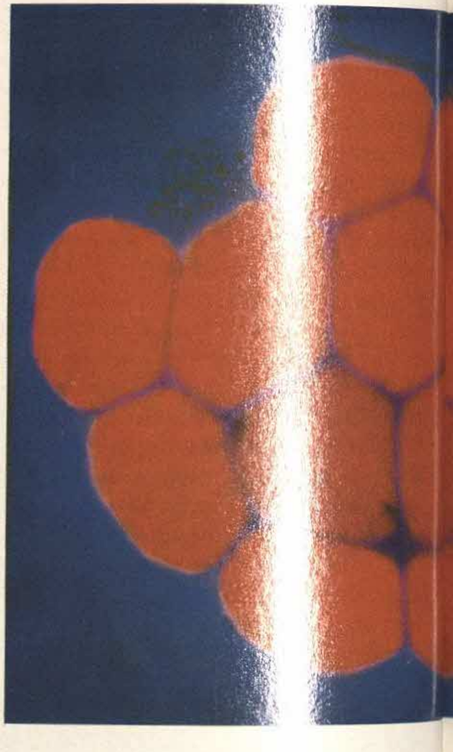
All matter is made up of elements. The tiniest particle of matter that can be divided and still retain its chemical identity is called a molecule. Molecules are formed when the atoms of one or more elements combine with atoms of either the same or different elements. Molecules containing more than a single type of atom create chemical compounds.

Cyclic compounds formed exclusively of carbon atoms, as in alicyclic and aromatic cyclic compounds, are called carbocyclic compounds. However, cyclic structures exist in which one or more of the atoms making up the ring are not carbon atoms. These atoms are called heteroatoms, and the compounds they form with carbon atoms are called heterocyclic compounds. Such substances are especially important because many natural compounds contain heterocyclic structures. Vitamins, indispensable to animal organisms; alkaloids, important for their applications in pharmacology; hemoglobin, from which blood receives its red coloring; vegetable colorants, such as chlorophyll, and the nucleic acids, on which heredity depends; all these are heterocyclic compounds. Many heterocyclic compounds, particularly colorants and pharmaceutical products such as vitamins, are produced synthetically on a large scale.

The variety of heterocyclic compounds is enormous and almost unlimited. Those of primary importance exist as a ring made up of five or six atoms. These rings contain nitrogen, oxygen, and sulfur as their heteroatoms. Synthesized compounds often contain selenium, phosphorus, arsenic, silicon, and other elements.

Heterocyclic rings may be saturated or unsaturated. The saturated rings have no special characteristics and their properties do not differ substantially from open-chain compounds. If an oxygen atom is present, the properties of the compound resemble those of an ether. If a nitrogen

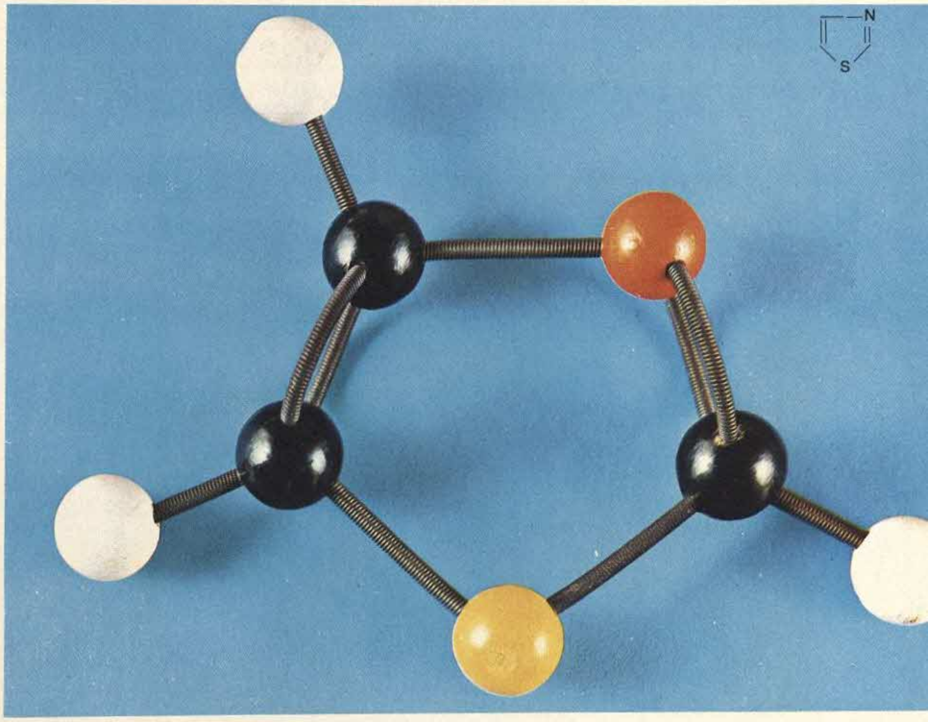
2



CHLOROPHYLL—Chlorophyll is one of the most important and abundant natural coloring agents, and is contained in the green parts of all plants. Its molecule has a complex structure and its nucleus is composed of a

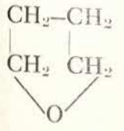
magnesium atom. Magnesium may share in the part chlorophyll plays in the assimilation process. Illustration 2 shows the chlorophyll contained in a seaweed. It appears red because it is seen through a fluorescing microscope.

3

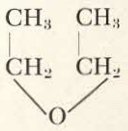


THIAZOLE—This heterocyclic ring is contained in penicillin, the important antibiotic discovered in the mold *Penicillium* by Fleming in 1928 and isolated by Chain and Florey in 1940. The heteroatoms are sulfur and nitrogen.

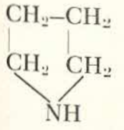
atom is present, the compound reacts as do the aliphatic amines.



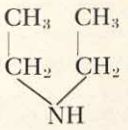
tetrahydrofuran



ethyl ether

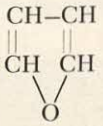


pyrrolidine

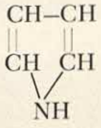


diethylamine

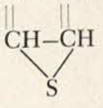
The main examples of unsaturated nuclei with conjugated double bonds are:



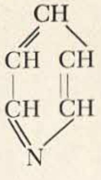
furan



pyrrole



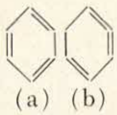
thiophene



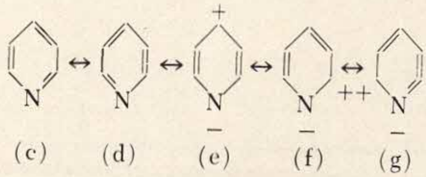
pyridine

AROMATICITY

The presence of conjugated double bonds gives these cyclic compounds the approximate stability of benzene. They have outstanding resistance to oxidizing agents and undergo substitution reactions instead of addition reactions. In other words, heterocyclic compounds may be typically aromatic. This can best be described by comparing a pyridine molecule with a benzene molecule. The real structure of benzene is neither (a) nor (b) but a hybrid resonance of



the two. The structure is particularly stable because all the carbon-carbon bonds are intermediate between a single and a double bond. Pyridine behaves similarly, but not identically. The presence of a nitrogen atom keeps the ring from being perfectly symmetrical, as in the case of benzene, and the resonance involves not only forms (c) and (d), corresponding to the two possible forms for benzene, but also the polar forms (e), (f), and (g). The pyridine molecule:



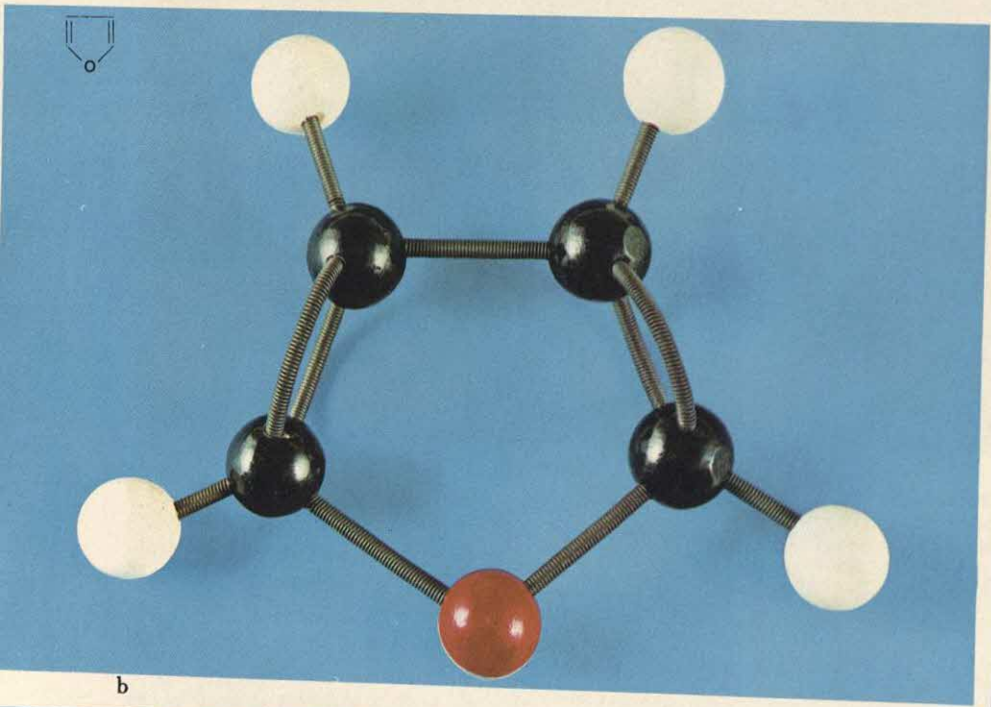
can be described as a resonance hybrid between five forms. (The double-headed arrow represents resonance.)

Interpretation of this phenomenon in pyridine is more difficult than in benzene. But, were this to be considered in terms of the polar forms, the existence of resonance, and therefore aromaticity, even in five-atom rings, can be justified.

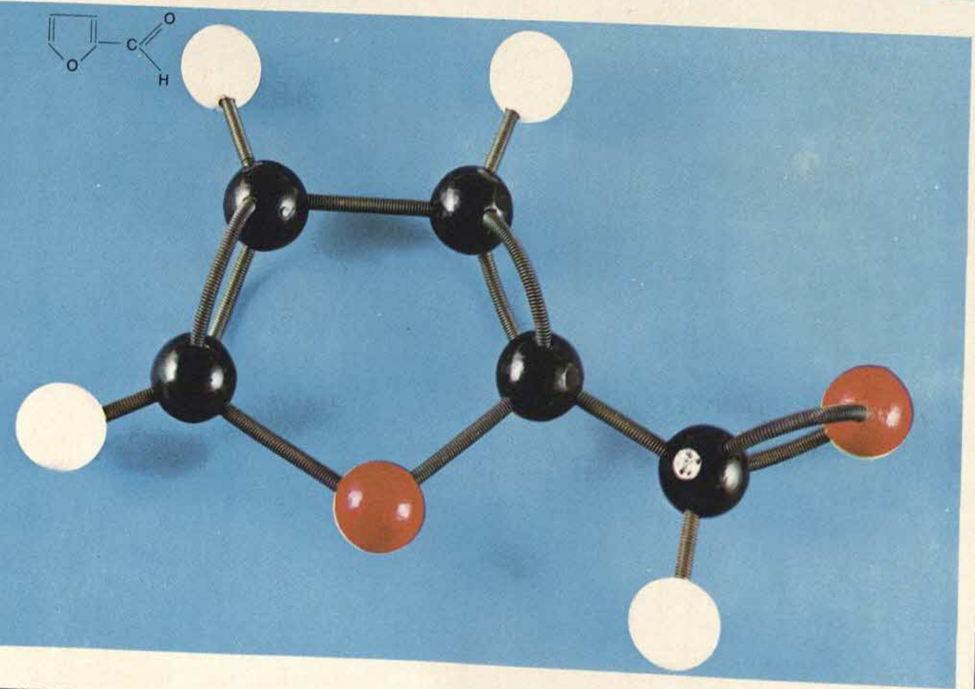
4

FURAN—Illustration 4a shows the simplest five-atom heterocyclic ring containing oxygen. It has two conjugated double bonds, which make it aromatic. Furan is a liquid that smells like chloroform. Industrially, furan is prepared from chaff, rice husks, or corncobs. These materials are made largely of pentosanes, that is, polymers of sugars with five carbon atoms (pentoses). The pentoses contain the structure of furan. By treatment with concentrated mineral acids, the pentoses provide furfural, the aldehyde of furan (Illustration 4b). Furfural produces furan when heated in the presence of catalysts. The furan ring appears naturally in numerous substances belonging to the carbohydrate series, the most important of which is sugar. By hydrogenating furan catalytically, tetrahydrofuran is obtained. It is widely used as a solvent and as a starting-point for one method of synthesizing nylon.

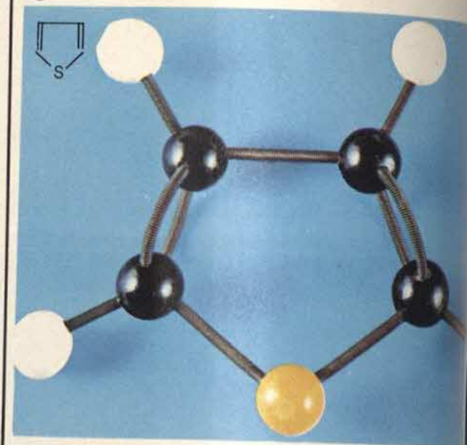
a



b

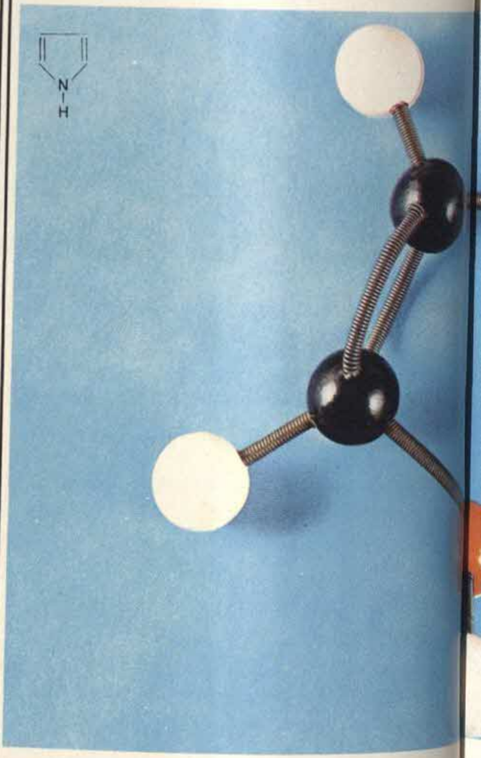


5

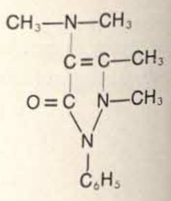


PYRROLE—The most important heterocyclic compound with five atoms is pyrrole. Its skeleton is found in many natural substances, such as hemin (the nonprotein part of hemoglobin), chlorophyll, and vitamin B_{12}, all of which have a typical cyclic structure in which four pyrrole rings are linked together around a metallic atom. Many derived substitutes of pyrrole are

6

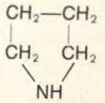


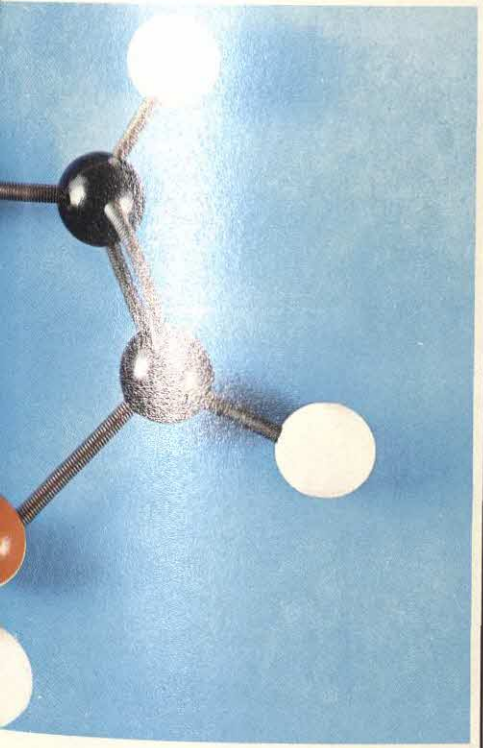
PYRAZOLE—This nucleus is studied in depth because of its importance in pharmaceutical and colorant fields. In particular, the pyrazolones, which are ketone derivatives of the hydrogenated product pyrazoline, are important as antipyretics.



THIOPHENE—The physical properties of this heterocyclic compound place it closest to benzene, which is obtained from coal tar. Benzene always contains a small amount of thiophene, which is formed through pyrolysis of the sulfurized slag of coal. Since the boiling point of the two liquids is so close that they cannot be separated by fractional distillation, chemical methods are used. A little thiophene is always present in commercial benzene. This can be shown with isatin in the presence of sulfuric acid, which yields a green-blue coloration. This reaction was once believed to be characteristic of benzene. The German chemist Victor Meyer used to demonstrate the reaction to his pupils. On one occasion, the coloration did not appear and Meyer discovered that the coloration was not due to benzene but to thiophene.

known and all show the reactions characteristic of the aromatic compounds. The hydrogenated derivative of pyrrole is pyrrolidine:





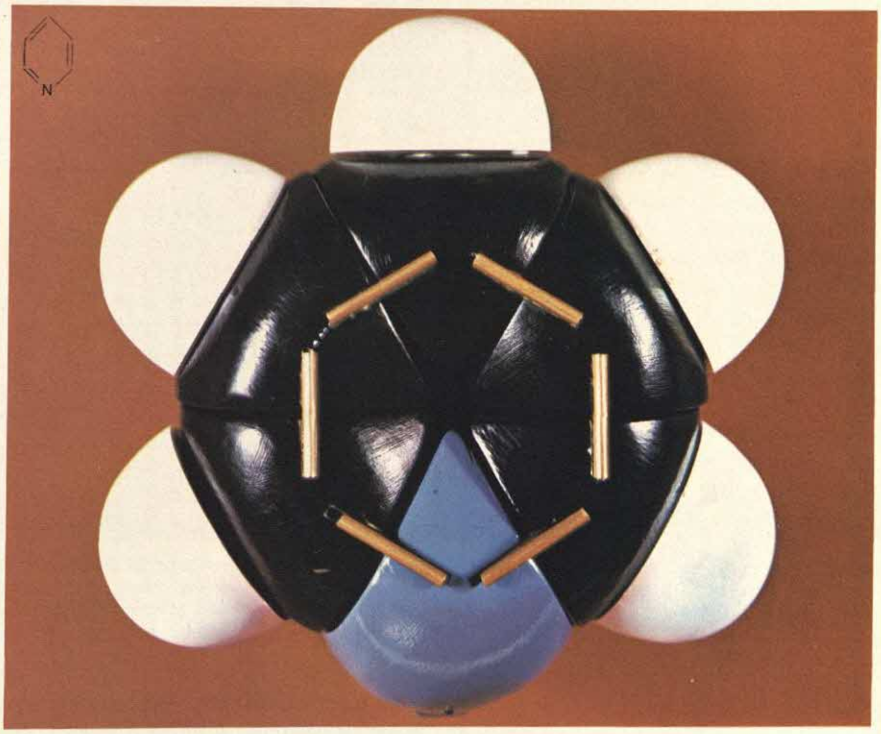
7

PYRIDINE — Heterocyclic compounds with hexatomic rings containing one or more heteroatoms vary in their aromaticity if the ring has three double bonds in conjugation. The heterocyclic ring derives from the benzene nucleus when one or more $-CH$ groups are replaced with heteroatoms. For example, if a single $-CH$ group is replaced with a nitrogen atom, pyridine results; with two nitrogen atoms, diazine (varying according to the position of the nitrogen atoms); with three, triazine, and so on. Pyridine is present in the first and second fraction of coal tar. As with benzene, the basic properties of pyridine allow it to be separated from the other compounds by exploiting its great solubility in a solution of sulfuric acid. Pyridine has a very unpleasant odor, which explains why it, and its derivatives, are used to denature ethyl alcohol.

Among the most important derivatives of pyridine is nicotinic acid, which is produced from nicotine, the alkaloid of tobacco. Its amide, nicotinamide, is vitamin PP, a pellagra-preventive factor. The diethylamide of nicotinic acid is nikethamide, which is used as a respiratory stimulant and for therapeutic purposes.

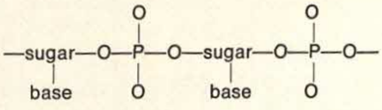
The completely hydrogenated product of pyridine is piperidine, $C_5H_{10}NH$, which is normally obtained by hydrogenating pyridine.

8



9

PYRIMIDINE—This is the most important hexatomic compound having two nitrogen atoms as heteroatoms. Thymine, cytosine, and uracil, derivatives of pyrimidine, have been researched extensively in the biological fields because these derivatives enter into the composition of nucleic acids which, combined with proteins in nucleoproteins, are integrating components and biologically important in the nuclei of cells. Many species of virus belong to the nucleoproteins. The complexity and size of these molecules is indicated by their molecular weight, which varies between 13 and 18 million. The nucleic acids control the transmission of inherited characteristics and protein synthesis, and are made up from pyrimidine or purine bases, sugars (riboses or deoxyriboses), and phosphoric acid linked in chains:



$$-\underset{\text{base}}{\underset{|}{\text{sugar}}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{P}}-O-\underset{\text{base}}{\underset{|}{\text{sugar}}}-O-\underset{\underset{O}{|}}{\overset{\overset{O}{|}}{P}}-O-$$

—nucleic acid unit—

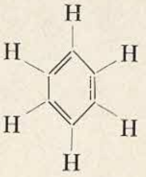
DNA is present in cell nuclei, and RNA in the nucleolus and cytoplasm of the cell.

THE POLYNUCLEAR AROMATIC COMPOUNDS

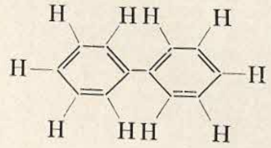
colorful rings of organic dyes

Early man discovered no doubt by accident that berry juices could be used to add color to an otherwise drab wardrobe. The dyeing of fabrics was known to the Persian, Indian, and Egyptian cultures centuries ago. Relying solely on vegetable dyes, these ancient peoples refined the techniques of dyeing into a fine art. It is unlikely, however, that they knew anything about the chemistry of dyes. Not until the late nineteenth century did chemistry progress to the point where laboratory analysis of organic compounds was possible. With subsequent refinements in organic synthesis, industries were born that owe their existence to the group of organic compounds known as polynuclear aromatic compounds. In addition to their use in modern dyes, these compounds are present in pharmaceuticals, insecticides, and plastics.

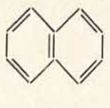
Compounds containing a six-carbon ring with three double bonds are known as aromatic compounds. The simplest of these is benzene, C_6H_6:



Molecules containing two or more systems of these rings are known as polynuclear aromatic compounds. There are numerous ways in which such rings can be joined, the simplest being a linkage where no carbon atoms are shared. The structure of diphenyl illustrates this:



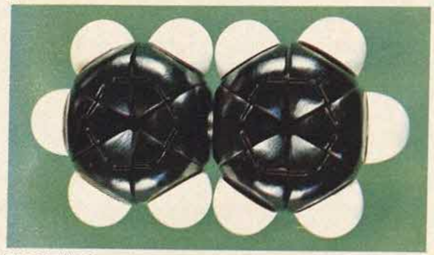
The distillation of coal tar provides large quantities of a second type of polynuclear aromatic compounds. This important class of hydrocarbons is those with condensed nuclei. Naphthalene



(hydrogens not shown)

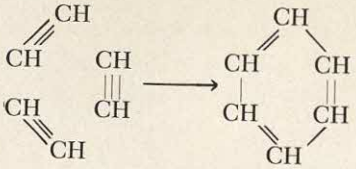
has two condensed benzene rings, and is a classic example of compounds significant in dye synthesis.

1

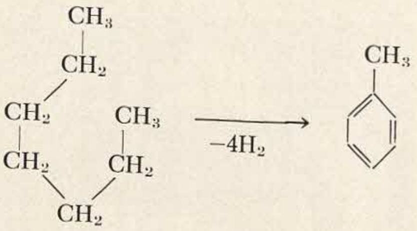


DIPHENYL—The polynuclear aromatic compounds are molecules containing a number of benzene rings. In diphenyl, two rings are linked without having a common carbon atom.

Most of these compounds, as such, are not found in coal. They are formed during the distillation of coal as a result of reactions taking place at high temperatures. For example, when linear compounds or compounds with an alicyclic structure are passed through heated coils, aromatic and polycyclic compounds are formed. Benzene itself can be prepared from acetylene in this very manner:



In modern industry, benzene derivatives are obtained in large quantities by the dehydrocyclization process. Heptane, when heated with appropriate catalysts, produces toluene:



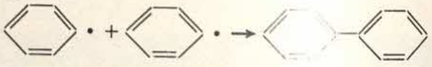
These examples show that linear molecules may join to form rings (cyclization). High temperatures and catalysts cause the electrons linking the molecules to vibrate. When the vibrations are strong enough to break the bonds, so-called radicals are formed. Methane provides a good example:

$$CH_4 \xrightarrow[\Delta]{} \cdot CH_3 + \cdot H.$$

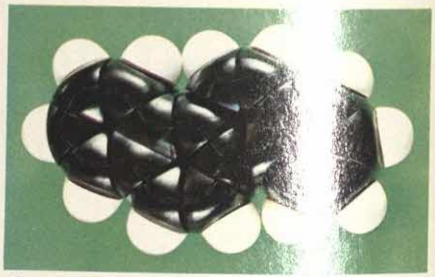
The small dots represent solitary electrons, and the delta sign (Δ) means that heat has been applied. Such radicals are extremely reactive (the carbon atom tends to reacquire four bonds) and are, therefore, quite unstable and short-lived. They may "disappear" by linking with a second radical to regain stability. Two methyl radicals, for example, react to form ethane:

$$\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3.$$

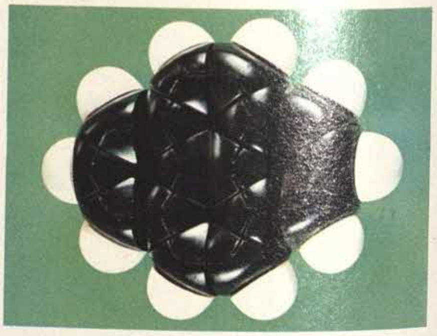
With cyclic compounds, the disappearance of the radicals in ring molecules leads to the formation of polynuclear compounds. The linking of two phenyl radicals results in the formation of diphenyl:



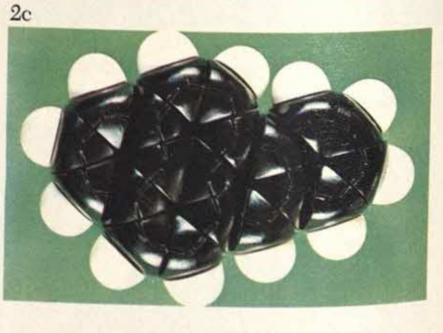
2a



2b

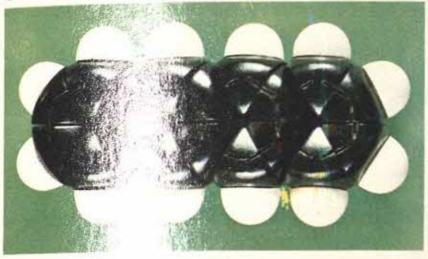


2c



POLYNUCLEAR COMPOUNDS—Found in coal tar, polynuclear compounds are formed by several condensed benzene rings. Illustration 2a shows the structure of chrysene, 2b that of pyrene, and 2c represents benzopyrene. The latter is found in tobacco smoke and has been shown to be carcinogenic.

3



TETRACENE—Linear compounds with several condensed benzene nuclei have been synthesized recently. One of these compounds is tetracene.

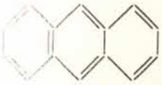
4

NAPHTHALENE—Naphthalene, another coal-tar distillation product, is used as a moth preventive. Naphthalene has the property of being able to go directly from the solid to the gaseous state. Illustration 4 shows the apparatus used in subliming naphthalene in the laboratory.

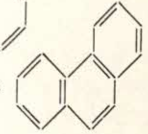
If the linkage provides two carbon atoms in common, naphthalene is the product.

Polynuclear compounds having three rings are:

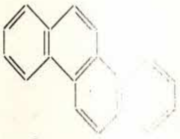
anthracene



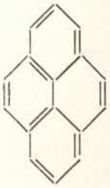
or phenanthrene



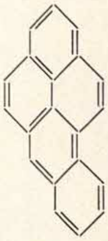
In coal tar, polynuclear compounds with several rings are chrysene, pyrene, and benzopyrene:



chrysene



pyrene

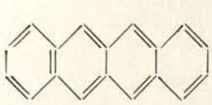


benzopyrene

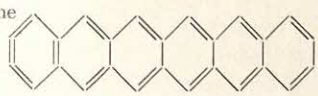
Benzopyrene has been isolated in cigarette smoke and is highly carcinogenic.

Compounds with several linearly condensed rings include:

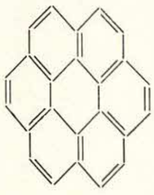
tetracene



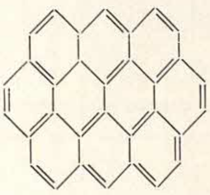
and hexacene



Two still more picturesque substances with a greater number of rings are coronene and ovalene:

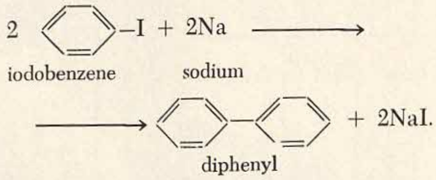


coronene

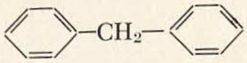


ovalene

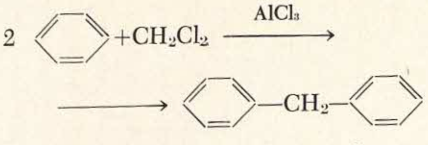
The reactions generated by heat are often uncontrolled, and hence are unsuitable for the synthesis of polynuclear compounds. But there are laboratory and industrial reactions that produce these substances. The Wurtz synthesis uses benzene derivatives in the production of diphenyl:



By replacing two hydrogen atoms in methane with two phenyl groups, the result is diphenylmethane:

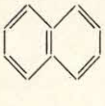


This compound can be produced in the Friedel-Crafts reaction from dichloromethane and two benzene molecules in the presence of aluminum chloride ($AlCl_3$):



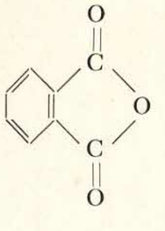
In addition, triphenylmethane and tetraphenylmethane have been produced in this way.

NAPHTHALENE



Naphthalene is made up of two condensed benzene nuclei. It is one of many coal-tar distillation products and is produced in the second distillation fraction. The substance is a white, crystalline solid having the property of being able to go directly from the solid to the gaseous state.

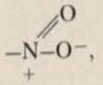
Naphthalene is used to combat clothes moths but is more widely used in the preparation of dyes and phthalic anhydride:



Phthalic anhydride is an important starting point for plasticizers, resins, dyes, and pharmaceutical products.

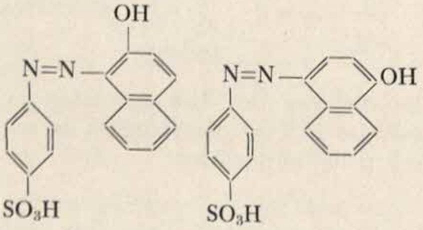
A function of the polynuclear aromatic compounds is their use as foundations in dye manufacture. This is because their molecules contain a large number of double bonds. A substance has a given color because it absorbs light waves of a certain frequency in the visible spectrum. Those frequencies not absorbed are reflected, giving the substance its color. Experiments have demonstrated that a compound's selective absorption of light is due in part to its state of unsaturation—the presence of double bonds. The double bonds of organic molecules possess the characteristic property of being able to absorb light. For example, under normal light benzene is colorless; it does absorb ultraviolet light, however, which is outside the visible spectrum.

By attaching a group containing double bonds, as in the nitro group, to ben-



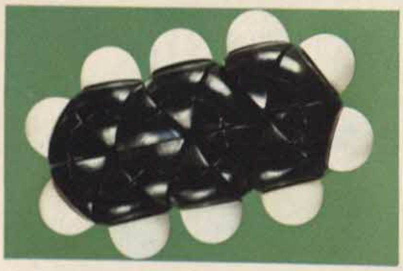
$$-\overset{+}{N}(=O)-O^-,$$

zene, a compound reflecting visible light results. In fact, nitrobenzene has a yellowish hue. The introduction of additional unsaturated groups, known as chromophores or color-bearers, produces substances having other color properties. Naphthalene, anthracene, and similar compounds are good examples of these chemicals from which dyes are derived. Orange-1 and Orange-2 are dyes containing the naphthalene nucleus:



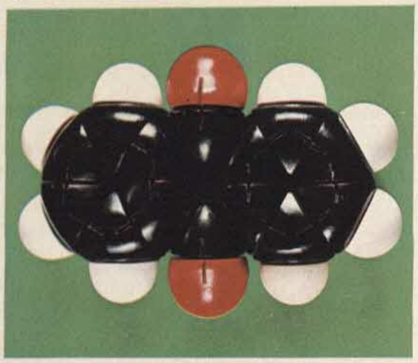
The −N=N− chromophore group (azogroup) forms a bridge between the naphthalene and benzene systems.

5

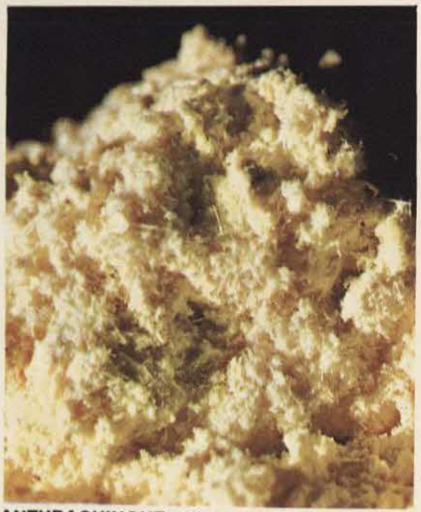


ANTHRACENE—Composed of three linearly condensed benzene rings, the compound anthracene is important in the preparation of dyes.

6a

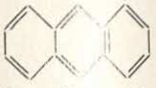


6b

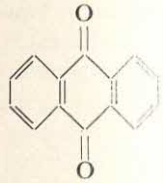


ANTHRAQUINONE—Illustration 6a depicts the structure of another important polynuclear aromatic compound. Anthraquinone is derived from the oxidation of anthracene, and its derivatives, especially the sulfonated compounds, are excellent dyes for wool and cotton. The soft, yellowish mass in Illustration 6b is solid anthraquinone.

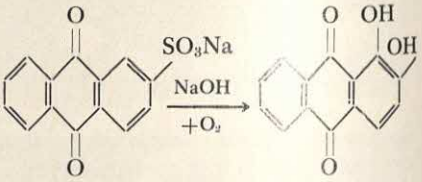
ANTHRACENE



Anthracene is another of the substances distilled from coal tar. It is purified by sublimation—a process of solidification that occurs when vapors contact a cold surface. Like naphthalene, it is a colorless substance. In addition, it is fluorescent and is widely used in dye preparation. The derivatives of anthraquinone,



the ketone obtained by oxidizing anthracene, are of primary importance to the dye industry. Special mention is made of the sulfonated derivatives. Alizarin, for example, is a glucoside found in madder root, one of the vegetable dyes of the ancients. Today, this compound is used for dyeing wool and cotton. It is synthesized from anthraquinonesulfonic acid through fusion with NaOH in the presence of an oxidizer:

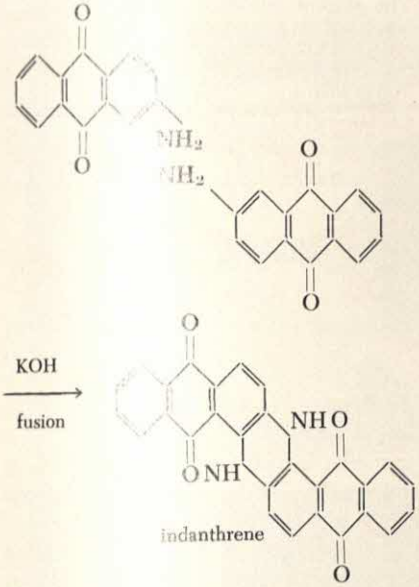


anthraquinonesulfonic acid

alizarin

Certain animal organisms also contain anthraquinone derivatives. Cochineal dye, an oxyanthraquinone, is found in the cochineal bug, a small plant parasite. Raised primarily in America and Mexico, the females are killed with steam before laying their eggs. Dried and ground to a powder, these insects provide one of the finest and most resistant dyes for silk and wool. The dyestuff is used to produce scarlet, crimson, orange, and other tints.

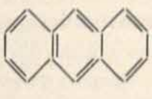
Indanthrene is a synthetic produced industrially by the fusion of two beta-amino-anthraquinone molecules with potassium hydroxide:

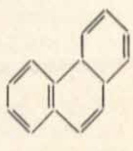


When discovered in 1901, indanthrene opened a new age for this group of dyes. A number of its derivatives are used to color both animal and vegetable fibers.

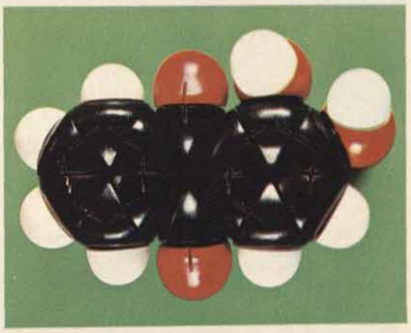
PHENANTHRENE

Phenanthrene differs from anthracene because its rings are linked at angles rather than linearly:

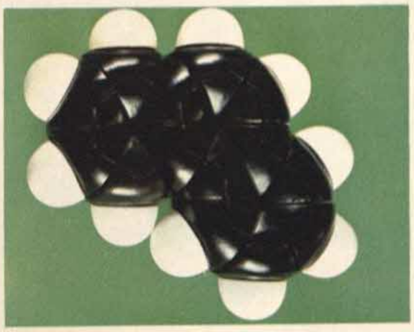

anthracene


phenanthrene

7a



8

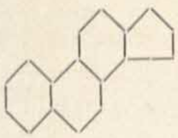


PHENANTHRENE—Also contained in coal tar, the compound phenanthrene differs from anthracene in that its rings are joined at angles. While phenanthrene does not have major industrial importance, it is used as an intermediary in the preparation of the alkaloid morphine.

7b

ALIZARIN—The structure in Illustration 7a is responsible for the series of colorful dyes shown in flasks in Illustration 7b. Alizarin, one of the vegetable dyes of the ancients, was prepared from madder root until 1868. It is now prepared synthetically.

While having little industrial importance, phenanthrene's derivatives include natural products such as the alkaloid morphine. Cyclopentanoperhydrophenanthrene,



includes a cyclopentane ring condensed with perhydrophenanthrene, a product of the complete hydrogenation of phenanthrene. It is the common basis of sterols, bile acids, and sex hormones—a family of natural compounds fundamentally important for human survival. Modern research has identified and produced several of these substances in the laboratory. Phenanthrene crystallizes as colorless leaflets. Its melting point is 101° C (about 214° F), and its boiling point is 332° C (629.6° F).

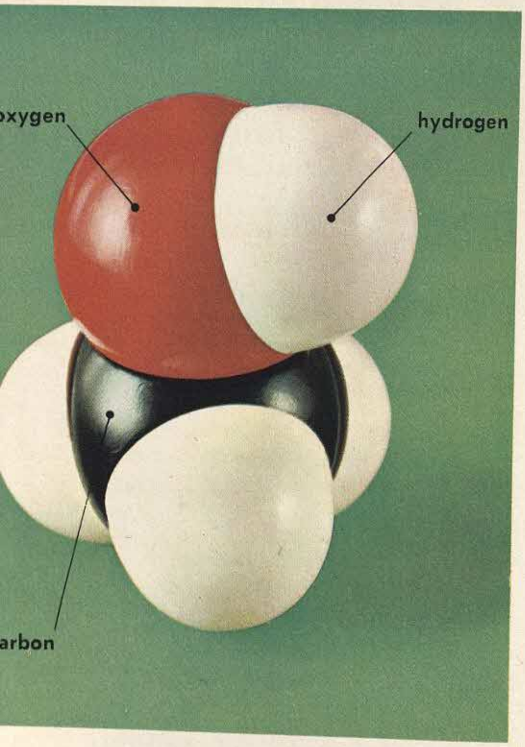
THE ALCOHOLS

the spirit in beer and wine

For untold years, man has fermented the sugary juices of fruits and grains to prepare alcoholic beverages for his celebrations, rituals, and medicines. Such drinks have been known to virtually all historic peoples, no matter how primitive; they include, among others, grape wines, wines from other fruits, hard cider, rice and palm wine, kumiss (fermented mare's milk), mead (from honey), and beer, which was probably first brewed from barley malt by the ancient Egyptians.

The art of distilling these drinks to obtain higher concentrations of alcohol is also very ancient. The Chinese distilled sutchoo from rice and millet wines about 1000 B.C. In Ceylon and India arrack was distilled from toddy as early as 800 B.C. Brandy was first made in Italy around A.D. 1000. The Arabs, meanwhile, had already become familiar with the process. They called volatile substances, suitable for boiling off and condensing, by a general name *al-kohl,* from which the word "alcohol" was derived.

1



METHYL ALCOHOL—Methyl alcohol is the simplest alcohol. In principle, it can be obtained by the replacement of a hydrogen atom in methane with an —OH group. The —OH group is characteristic of the alcohols and determines their properties. Once made exclusively by the dry distillation of wood, methyl alcohol is also known as "wood alcohol."

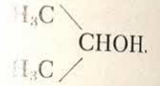
The alcohol of alcoholic beverages is chemically known as ethyl alcohol, or ethanol, CH_3CH_2OH. It is a member of a group of organic compounds known as the alcohols, whose characteristic is that a hydroxyl group, $-OH$, is firmly bound to the carbon atom. Unlike the alkaline hydroxyl group that is associated with inorganic bases, this group does not ionize in water. In fact, the pH of alcohols is neutral; they are neither acid nor base. The simplest alcohol is methyl alcohol, or methanol, CH_3OH, also called wood alcohol.

In principle, alcohol synthesis is relatively straightforward because these compounds are hydrocarbon derivatives in which a hydrogen atom is replaced by the $-OH$ group. For example, methyl alcohol, CH_3OH, is obtained by replacing a hydrogen atom in methane, CH_4, with an $-OH$ group. Ethyl alcohol, CH_3CH_2OH, results in the same way from ethane, $CH_3{-}CH_3$.

With methane and ethane as "parent" compounds for alcohols, only one "form" of the product is possible. As more and more hydrocarbon units are added to the hydroxyl group, however, the resultant alcohols can assume additional configurations. A case in point is the next alcohol in the series: propyl alcohol. The parent substance here is propane, $CH_3{-}CH_2{-}CH_3$, and the $-OH$ group can replace a hydrogen atom in either a methyl group, $-CH_3$, or the methylene group, $-CH_2$. In the first instance, the product is normal propyl (*n*-propyl) alcohol, and in the second isopropyl alcohol:

$CH_3{-}CH_2{-}CH_2OH$

n-propyl alcohol



$$\begin{matrix} H_3C \diagdown \\ \quad CHOH. \\ H_3C \diagup \end{matrix}$$

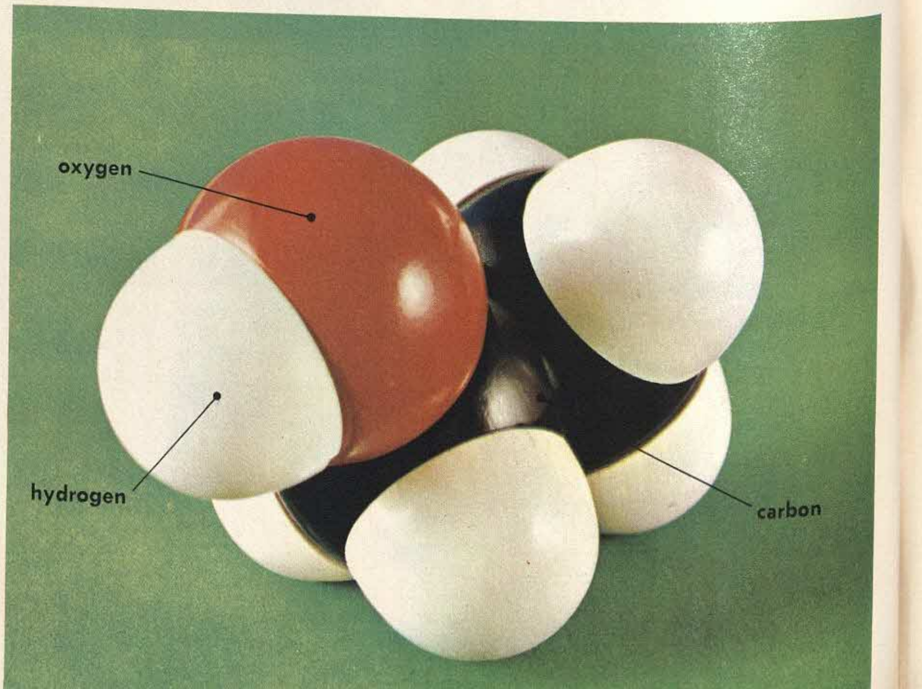
isopropyl alcohol

As the number of hydrocarbon units in an alcohol increases, there is a corresponding increase in the possibilities for linking the $-OH$ group to other carbon atoms besides the terminal ones.

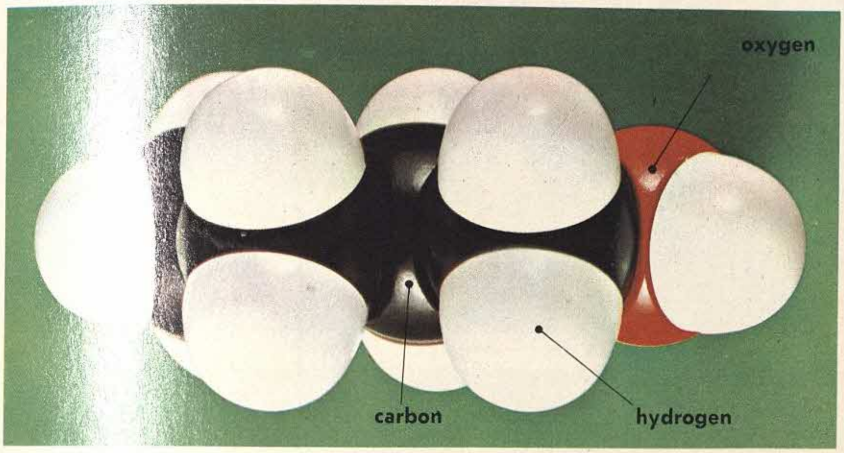
An $-OH$ group that is attached to a terminal carbon atom of a hydrocarbon chain is called a primary alcohol—that is, the carbon atom to which the hydroxyl group is associated is linked with only *one* other carbon atom. In isopropyl alcohol the hydroxyl associated carbon atom is linked to *two* other carbon atoms; therefore, isopropyl alcohol is called a secondary alcohol. The hydroxyl group may also be associated with a tertiary carbon atom, or one linked to *three* other carbon atoms; alcohols that exhibit this characteristic are called tertiary alcohols. An example is found in the isomers

ETHYL ALCOHOL—Second simplest in the series of alcohols, ethanol is one of the most important. Known since antiquity, ethanol is a product of carbohydrate fermentation. Sugars such as glucose and fructose, common to fruit juices, are easily broken down by fermentation enzymes into ethyl alcohol and carbon dioxide.

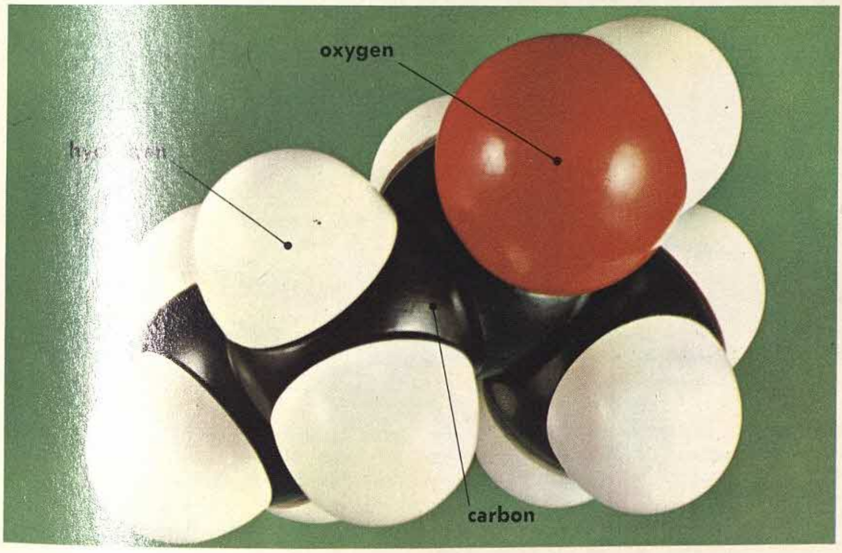
2



3a

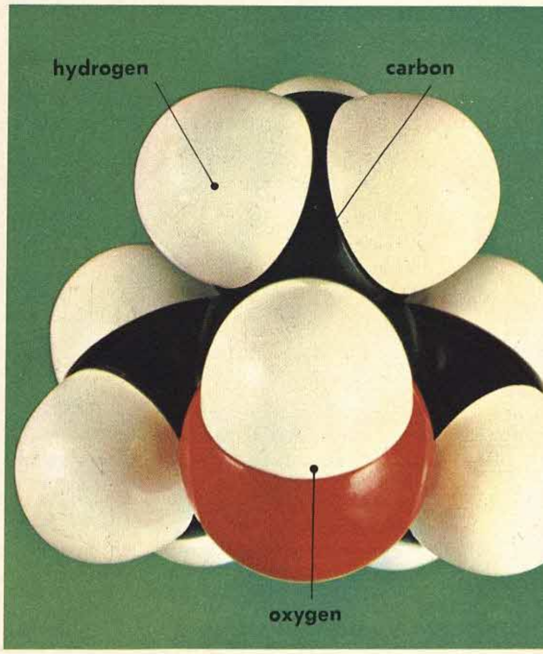


3b

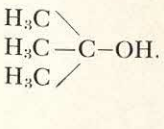


BUTYL ALCOHOL—Depending on which hydrogen atom is replaced by the —OH group, an alcohol is termed primary, secondary, or tertiary. Illustration 3a shows the structure of primary butyl alcohol (also called normal-butyl alcohol), with its —OH group linked to a carbon atom at one end of the hydrocarbon chain. The secondary butyl alcohol in Illustration 3b shows that the hydroxyl group is bonded to a carbon atom in the middle of the chain. Tertiary butyl alcohol has the —OH linked to a carbon atom that, itself, is linked to three other carbon atoms, as in Illustration 3c.

3c



of butyl alcohol; *n*-butyl alcohol is $CH_3CH_2CH_2CH_2OH$. Another isomer, where the —OH is linked to the second carbon atom and thus forms a secondary alcohol, is immediately evident; it is $CH_3CH_2CH(OH)CH_3$, or *sec*-butyl alcohol. Another primary alcohol in which one CH carbon is linked to three other carbon atoms, CH_3, CH_3, and CH_2OH, is isobutyl alcohol. If in this starlike configuration of hydrocarbon units the hydroxyl group is associated not with a terminal carbon atom but with the central one, the resulting tertiary alcohol is *ter*-butyl alcohol,



$$(H_3C)_3C-OH.$$

There are also polyvalent alcohols, which contain two or more hydroxyl groups per molecule. Examples are ethylene glycol, $HOCH_2CH_2OH$, and glycerol, $HOCH_2CH(OH)CH_2OH$. In such cases, there is never more than one hydroxyl group associated with the same carbon atom, for the *gem*-diol group, $>C(OH)_2$, is unstable; under normal conditions it loses water, HOH, to become $>C{=}O$, the carbonyl group.

PROPERTIES

The properties of the alcohols differ according to the number and arrangement of carbon atoms in the molecule. Solubility in water illustrates this point: the "lower" alcohols, such as methyl and ethyl alcohol, mix easily with water because few carbon atoms are present in the molecule. With an increase in the number of carbon atoms, the influence of the hydrocarbon residue becomes greater. For this reason, the "higher" alcohols, such as heptyl alcohol, become more like the corresponding hydrocarbons, with a decreasing solubility in water. In addition, methyl and ethyl alcohol, for instance, react to sodium in much the same way as water, though less strongly. These alcohols produce true salts:

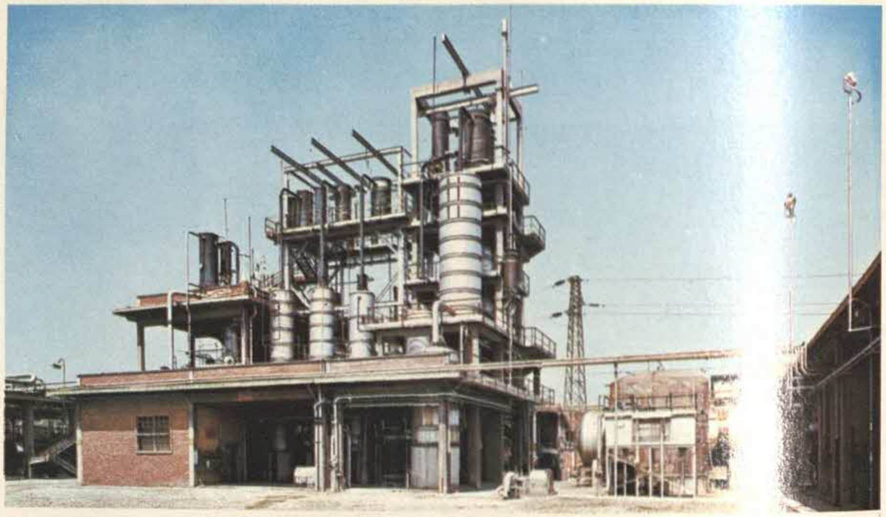
$$CH_3{-}OH + Na \rightarrow CH_3ONa + 1/2H_2$$

$$CH_3{-}CH_2{-}OH + Na \rightarrow CH_3{-}CH_2ONa + 1/2H_2.$$

With the higher alcohols, though, this

4a

4b

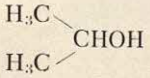
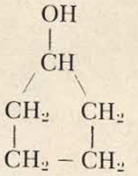
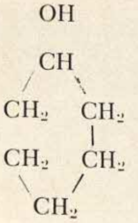
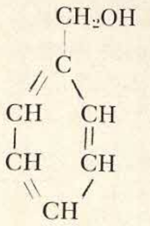


INDUSTRIAL PLANTS—The alcohols are widely used industrially. Illustration 4a shows the gleaming copper stills in a section of a liqueur-producing plant. The containers are used for distilling herb and spice essences with ethanol. Methanol is produced on a large scale in modern plants like that in 4b.

reaction is not as readily obtained.

Though alcohols can be considered as derived from hydrocarbons by simple replacement of a hydrogen atom with the −OH group, not all hydrocarbons with hydroxyl attached are alcohols. Notable exceptions are aromatic hydrocarbons, such as benzene and its derivatives. In fact, benzene with an −OH group attached is phenol, whose properties are quite different from those of alcohols.

The alcohols may be saturated, unsaturated with double and triple bonds, or cyclic. The most accurate way to name alcohols is by adding an -ol suffix to the name of the parent hydrocarbon. Thus:

CH_3OH	methanol (methyl alcohol)
CH_3CH_2OH	ethanol (ethyl alcohol)
$CH_3CH_2CH_2OH$	propanol (*n*-propyl alcohol) (1-propanol)
	isopropanol (isopropyl alcohol) (2-propanol)
	cyclopentanol (cyclopentyl alcohol)
	cyclohexanol (cyclohexyl alcohol)
$CH_2{=}CH{-}CH_2OH$	2-propenol (allyl alcohol)
$CH{\equiv}C{-}CH_2OH$	2 propyn-1-ol (propargyl alcohol)
	alpha-hydroxy toluene (benzyl alcohol)

SOURCES AND FORMATION

Alcohols are common outside the laboratory. Small quantities of ethyl and methyl alcohol are found in the free state in plants. The higher alcohols are very common in nature. Menthol, a cyclical alcohol related to cyclohexane, is present in mint plants and is responsible for their characteristic fragrance. Esters, produced by the condensation of alcohols and organic acids, with elimination of a water molecule formed by the OH of the organic acid's carboxyl group, $-C{=}O(OH)$, and the hydrogen of the alcohol's hydroxyl group, occur naturally in plant oils. The scents of fruits are caused by these compounds. Esters derived from the higher alcohols are essential ingredients in natural waxes.

In much the same way that they can be synthesized, esters can be broken down into their acid and alcohol components (the esterification reaction is an equilibrium reaction). This is one way of obtaining alcohols from the natural esters in fruit essences and wax.

A very important way to form many lower alcohols is to ferment carbohydrates. When treated with complex molecules called enzymes (present in yeasts and other microorganisms) carbohydrates ferment in a relatively short time. Natural sugars, such as glucose and fructose, common ingredients in fruit juices, are easily converted to ethyl alcohol and carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2.$$

Wine and beer are produced in this manner.

Chemical methods, on the other hand, use exchange or reduction reactions. For instance, when a halogenated hydrocarbon is treated with sodium hydroxide, the halogen and hydroxyl are exchanged:

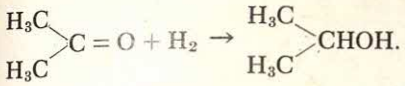
$$CH_3Cl + NaOH \rightarrow CH_3OH + NaCl.$$

methyl chloride + sodium hydroxide → methanol + sodium chloride

If aldehydes and ketones are reduced, the result is an alcohol:

$$CH_3CHO + H_2 \rightarrow CH_3CH_2OH.$$

acetaldehyde + hydrogen → ethanol



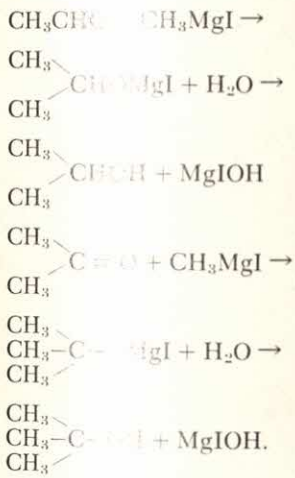
$$\begin{matrix}H_3C\\ \quad\end{matrix}\!\!>\!C=O+H_2\rightarrow\begin{matrix}H_3C\\ H_3C\end{matrix}\!\!>\!CHOH.$$

acetone + hydrogen → isopropanol

In a common laboratory reaction, a ketone or an aldehyde is reacted with alkylmagnesium halides. These are produced in the reaction between magnesium and a halogenated hydrocarbon:

$$\underset{\text{methyl iodide}}{CHI_3}+\underset{\text{magnesium}}{Mg}\rightarrow\underset{\text{methylmagnesium iodide}}{CH_3MgI.}$$

When added to aldehydes and ketones, they give products that break down into alcohol and a basic magnesium halide.



$$\begin{aligned}&CH_3CHO+CH_3MgI\rightarrow\\&(CH_3)_2CHOMgI+H_2O\rightarrow\\&(CH_3)_2CHOH+MgIOH\\&(CH_3)_2C=O+CH_3MgI\rightarrow\\&(CH_3)_3C-OMgI+H_2O\rightarrow\\&(CH_3)_3C-OH+MgIOH.\end{aligned}$$

5

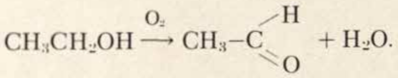
SODIUM ETHYLATE—Methyl and ethyl alcohol behave much like water with respect to metallic sodium. Reacting less strongly than water, these alcohols nevertheless produce solutions that are true salts. Illustration 5 shows that ethyl alcohol and sodium have reacted to form sodium ethylate (floating on the surface of the liquid).

6

BERGAMOT ORANGE—Esters can be found in plant oils, and the distinctive aroma of fruit is generally due to these compounds. Esters can be broken down to yield alcohols. The Bergamot orange contains an alcohol used in the perfume industry.

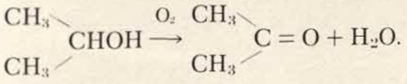
CHEMICAL BEHAVIOR

A reaction that differentiates primary, secondary, and tertiary alcohols is their behavior in the presence of oxidizing and dehydrogenating agents. The primary alcohols oxidize to aldehydes that, in turn, oxidize to carboxylic acids:



$$CH_3CH_2OH\xrightarrow{O_2}CH_3-C\begin{matrix}\diagup H\\ \diagdown O\end{matrix}+H_2O.$$

By either oxidation or dehydrogenation, the secondary alcohols form ketones with an equal number of carbon atoms:



$$\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!CHOH\xrightarrow{O_2}\begin{matrix}CH_3\\ CH_3\end{matrix}\!\!>\!C=O+H_2O.$$

Tertiary alcohols, however, resist oxidation, and, when oxidized, break down into acids and ketones having fewer carbon atoms.

The esterification reaction between acids and alcohols produces esters. This normally slow reaction can be accelerated by introducing small amounts of inorganic acids that act as catalysts:

$$CH_3COOH+CH_3CH_2OH$$

acetic acid + ethyl alcohol

$$\xrightarrow{H_2SO_4}CH_3C{=}O(OCH_2CH_3)+H_2O.$$

→ ethyl acetate + water

The esters of higher fatty acids with glycerol, $HOCH_2CH(OH)CH_2OH$, are called glycerides.

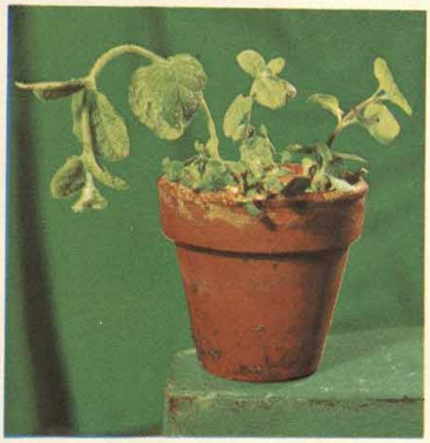
METHYL ALCOHOL

Methyl alcohol, or methanol, is the simplest of the alcohols and has many industrial uses. At one time, this compound was produced by the dry distillation of wood; hence the name "wood alcohol." In this process, green wood was heated in large iron boilers while the resulting vapors condensed in cooling coils. The liquid was allowed to separate into an oily layer and a watery mixture of methyl alcohol, acetic acid, and acetone. By washing this mixture in hot calcium hydroxide (quicklime), the acid was removed as a calcium salt. The methyl alcohol and acetone were recovered by distillation. Today, methanol is produced by reducing carbon monoxide with hydrogen in the presence of metal oxide catalysts,

$$CO+2H_2\xrightarrow{ZnO}CH_3OH$$

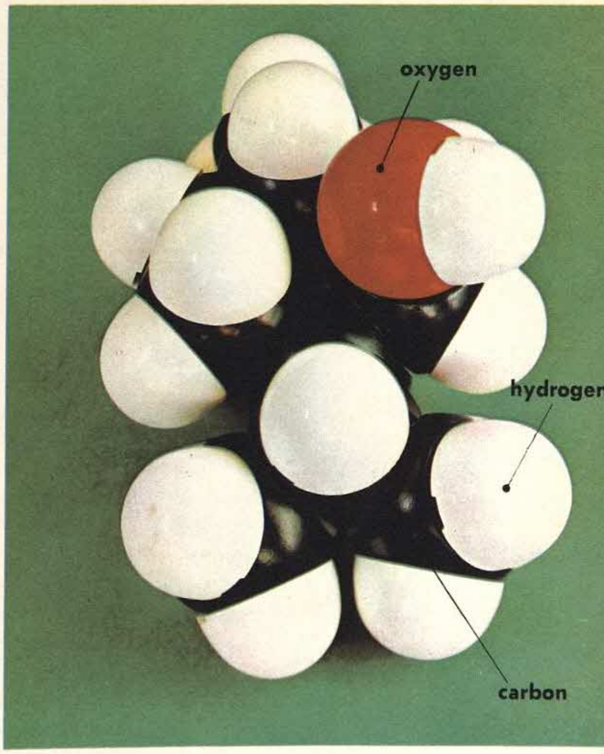
at very high pressures and temperatures.

7a



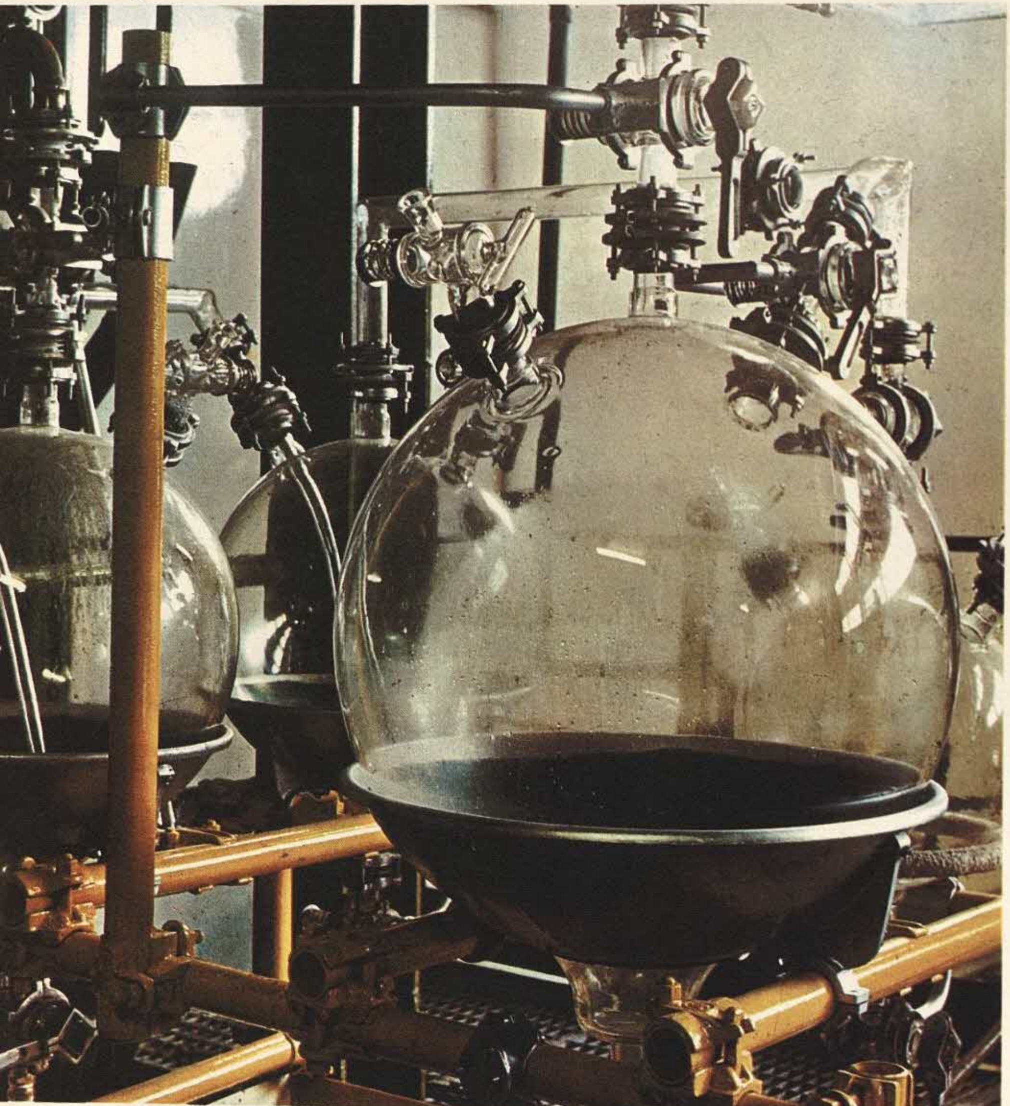
HIGHER ALCOHOLS—The alcohols are very common in the vegetable kingdom. The presence of large quantities of menthol in the mint plant (Illustration 7a) is responsible for mint's characteristic scent. Menthol, whose structure is illustrated in 7b, is an alcohol derivative of cyclohexane.

7b



ETHYL ALCOHOL | the inflammable principle hidden in sugar

1



THE PRODUCTION OF HIGH-PURITY ALCOHOL—The large glass flasks shown in this photograph are part of the equipment used in distilling alcohol having a high degree of purity. The flasks are similar to those used in many chemical laboratories, although larger.

When people speak of alcohol, they are generally referring to ethyl alcohol. Wide usage has confirmed it as the alcohol *par excellence,* underlining its enormous industrial and practical importance. Its existence was recognized as early as the eleventh century A.D., even if only on the fringes of legend. Aristotle, Hippocrates, and Pliny all spoke of a spirit of wine—an inflammable substance they claimed was the essence of this noble drink. It was not until many centuries later that alchemists isolated alcohol from wine by using techniques similar to those of present-day distillers.

The generally accepted derivation of the word alcohol is from the Arabic *kuhl, koh'l,* or *kohol,* meaning a "very fine powder." Gradually the word came to mean "essence" and Paracelsus defined it in the sixteenth century as "the most subtle part of anything." "Ethyl" refers to the fact that this particular alcohol can be converted to ethyl ether.

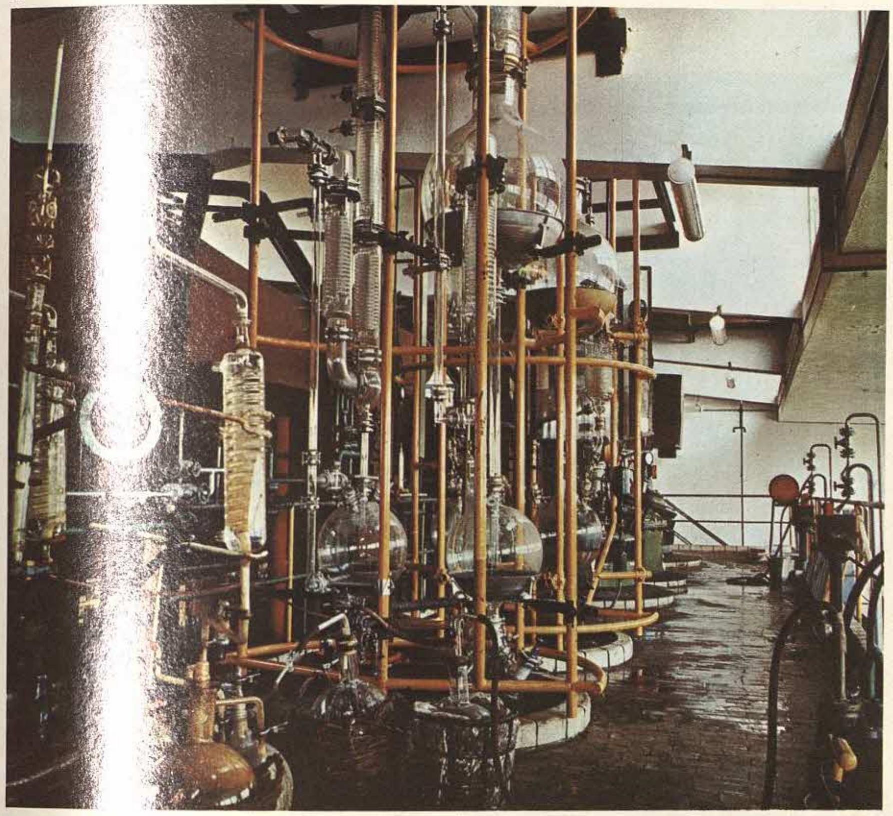
AN OLD WINE CELLAR—The slow process of fermenting wine takes place in these huge wooden barrels.

2

APPARATUS FOR DISTILLATION BY STEAM—In the foreground is a boiler that produces steam. Beyond it to the right is the double stopcock that admits steam to two different flasks, allowing a double distillation.

3

4



DISTILLATION OF ALCOHOL—Ethyl alcohol is being purified in this distilling plant. In various degrees of purity, ethyl alcohol is one of the most commonly used reagents in chemical laboratories.

From the chemical point of view, ethyl alcohol is the hydroxyl derivative of ethane; if an OH group is substituted for one part hydrogen in the hydrocarbon the result is ethyl alcohol, also called ethanol. The formula is as follows:

$$CH_3-CH_2-OH$$

The uses of ethyl alcohol are many and varied. Besides being an ingredient of all alcoholic beverages, it is used as a base for a great many products, such as acetaldehyde, as well as in a number of pharmaceutical derivatives, and as an ingredient in perfumes and cosmetics. Ethanol is used as rubbing alcohol and for sterilizing surgical instruments. Some of the chemicals derived from it include ether, used as an anesthetic; glycol ethers, used as solvents; esters such as ethyl, butyl and amyl acetates; and ethyl chloride (chloroethane). In mid-twentieth century, U.S. production figures for ethanol showed an annual output of between 400 million and 500 million proof gallons.

INDUSTRIAL SOURCES, BIOLOGICAL METHODS

Industry uses both biological and chemical methods to manufacture alcohol. Sugar-yielding products, such as beets, cereals, potatoes, and the by-products of the paper industry, are used as raw materials in this process. The starch from these products is converted into fermentable sugar by a preliminary treatment with malt. For fermentation to take place, the sugar must be composed of simple molecules.

Cereals and potatoes contain starch, a polymer of simple sugar, which must be broken down into single units before fermentation. The agent used to break down the chains of starch into molecules of glucose is an enzyme called diastase, obtained from malt. The same result may be obtained by subjecting the starch to an acid hydrolysis. This process is used to obtain simple sugar from cellulose residues of paper industry by-products.

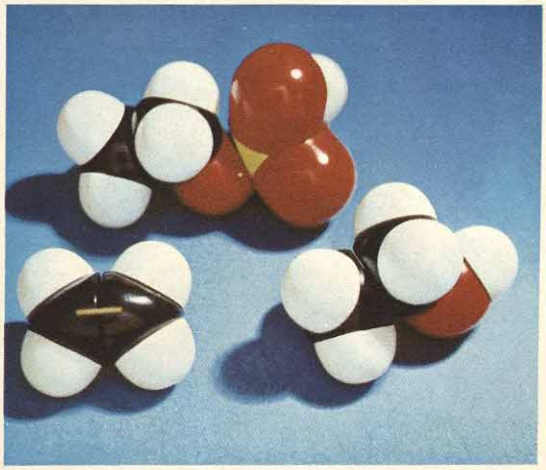
The transformation of sugar into alcohol is accomplished with yeasts—microscopic fungi. The following formula is a synthesis of the long and complex transformation:

$$\underset{\text{sugar}}{C_6H_{12}O_6} \xrightarrow{\text{yeasts}} \underset{\text{ethyl alcohol}}{2C_2H_5OH} + 2CO_2.$$

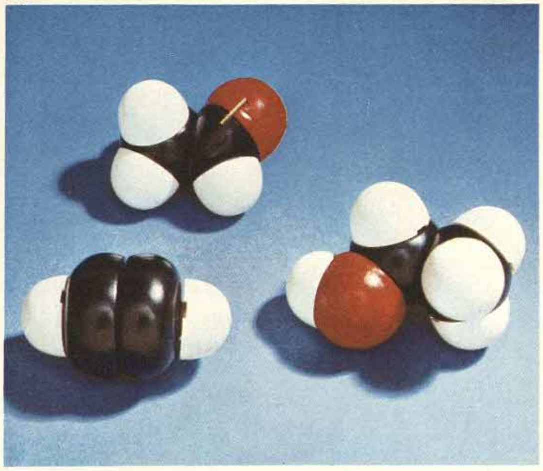
The complexity of the transformation is illustrated by the fact that fermentation requires as many as 12 different types of enzymes, producing that many intermediate products before the final creation of ethyl alcohol and carbon di-

PRODUCTION OF ETHYL ALCOHOL—Compact models of molecules (Illustration 5a) represent the reaction leading to the formation of ethyl alcohol from ethylene, through the formation of an intermediate compound of sulfuric acid. Ethyl alcohol can also be prepared from acetylene passing through acetaldehyde, as shown in Illustration 5b.

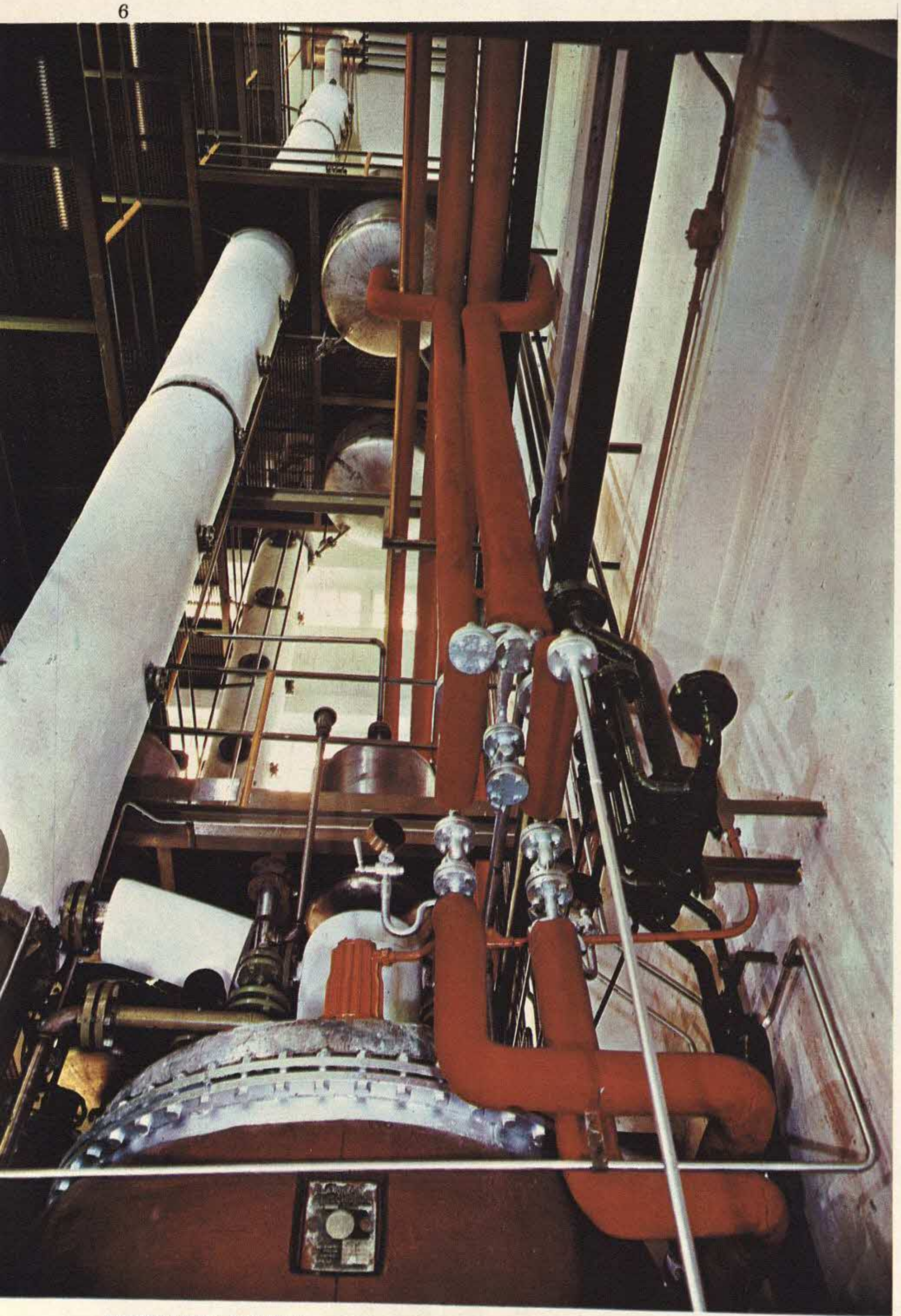
5a



5b



6



DISTILLATION COLUMN — Shown here is an industrial purification plant using distillation. Inside the column are perforated plates that increase the surface in contact with the vapor, thereby enabling the components of the mixture to be more easily separated.

oxide. After fermentation, alcohol is separated from the rest of the solution by distillation.

Fermentation does not produce a strong concentration of alcohol. Twenty percent of alcohol is the average result; a larger percentage inactivates the microorganisms that initiate the process.

INDUSTRIAL SOURCES CHEMICAL METHODS

Countries with good supplies of coal or petroleum use chemical methods to obtain alcohol. Ethylene, which is obtained from the cracking of petroleum or from the distillation of coal tar, is an example of this synthesis:

$$\underset{\text{ethylene}}{CH_2=CH_2}\xrightarrow[H_2O]{H_2SO_4}$$

$$CH_3-CH_2\,O\,SO_3H\longrightarrow$$

$$\longrightarrow\underset{\text{ethanol}}{CH_3CH_2OH}$$

Ethanol may also be obtained by a process called *synthol,* whereby a mixture of hydrogen and carbon dioxide is passed through the proper catalysts, usually chromium oxide and zinc oxide, at a temperature of 350-400° C (662-752° F). This process is used on a vast scale by industry.

ANHYDROUS OR ABSOLUTE ALCOHOL

Distillation is the process by which pure alcohol is separated from the other ingredients after fermentation. The product being distilled boils at a constant temperature and composition and is called an azeotropic mixture; it is composed of 95 parts alcohol to one of water. To obtain 99.9 percent pure alcohol, chemical means must be used to break the azeotrope. This is accomplished by dehydrating substances such as barium, calcium or aluminum oxides, or anhydrous copper sulfate. A third substance, benzene, which acts as an entrainer, is used in the distillation. A three-sided azeotrope is then formed, composed of

7

FERMENTATION VATS FOR BEER—These copper vats are used to ferment a liquid extract of barley with hops added. The liquid is subjected to controlled conditions of agitation and temperature.

8

PLANT FOR PRODUCING SYRUPS—Fruits and flowers are used to make linctus and other syrups, which are transformed into alcohol by fermentation.

The illustration shows part of a large pharmaceutical works where linctus (a throat medicament) is produced. In the middle are the autoclaves used for the process; they are equipped with systems for regulating pressure and temperature.

alcohol, water, and benzene, which boils at 65° C (149° F). When all the water has been removed, the product distilled is anhydrous alcohol at 78° C (172° F).

ALCOHOLIC BEVERAGES

The raw materials used to make wines are grapes and ciders of other fruits. Such wines are quickly made, for they require only the natural processes of fermentation and maturing. On the other hand, beverages with a high alcohol content require distillation from the fermented products.

Cognac is derived from the dregs of pressed grapes; brandy is made from the juices of fruits, particularly cherries. Rum is made from sugarcane; whiskey comes from corn or other kinds of grain rich in starch. As many varieties of whiskey are made as there are kinds of grain or malt. Juniper berries and aromatic herbs are used to make gin. Wheat, rye, corn, potatoes, sugar beets, or a combination of several of these, are the basis for vodka.

Liqueurs or cordials are the brightly colored, fragrant, and sweetened members of the family of distilled spirits. Developed originally during the middle ages by physicians and alchemists, they were touted as medicinal remedies, love potions, and general cure-alls. They have been known as oils, balms, and elixirs as well as liqueurs and cordials. The variety of colors, flavors, and combinations is practically limitless. The one factor that makes them all cordials is their sugar content; under U.S. regulations, a cordial must contain more than 2½ percent of sugar, but all cordials contain considerably more. They are divided into two groups—those with generic names, which are produced in all parts of the world, and those with proprietary brand names, which are produced by the trade-mark owner, such as Benedictine and Chartreuse, and are made only at their places of origin.

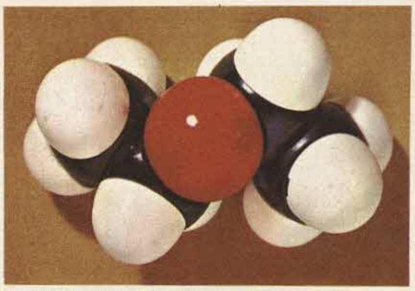
The quality and characteristic taste of all these beverages are determined by the various secondary products that form along with the alcohol during fermentation, or that distill with the alcohol. These include aldehydes, higher alcohols, fatty acids, and, above all, esters—the substances that carry aromas.

Alcohol in large quantities cannot be properly metabolized by the body; that is, it cannot be changed rapidly into carbon dioxide and water, and thus eliminated. An excess of alcohol damages the tissues, especially those of the liver, and also does injury to the central nervous system.

ETHERS | solvents and anesthetics from organic chemistry

To the average individual, ether evokes visions of hospitals, surgeons, and gleaming operating rooms. This volatile, flammable liquid has long enjoyed use as an agent to render the surgical patient unconscious. The first public demonstration of the anesthetic use of ether vapors in surgery was made by a Boston dentist in 1846. It remains one of the most widely used general anesthetics.

1



DIETHYL ETHER—This is the most important compound in the ether series. It is sometimes given the name "sulfuric ether" because it can be produced by dehydrating ethyl alcohol with sulfuric acid. Diethyl ether is highly volatile and flammable and must be handled and stored with care. Manufactured on a large scale, the compound is used mainly as a solvent and general anesthetic.

The word ether, or aether, is derived from an ancient Greek word meaning "air," and especially the bright, upper air. Ancient philosophers speculated that a weightless, fluid kind of matter prevailed in the Heavens and called it ether (hence, ethereal beings). Later, alchemists called very volatile materials ethers, perhaps relating them to the celestial matter. Prominent among these ethers was the light, vaporizing liquid obtained by distilling spirit of wine (alcohol) with oil of vitriol (concentrated sulfuric acid), still known as ether. Today's chemists classify ether (or, more properly, diethyl ether) as a member of a group of organic compounds with similar structures and properties, called the ethers.

Independently, seventeenth-century physicists postulated the existence of a weightless fluid, ether, filling all space. This ether, unrelated to the ether of the chemist, accounted for many puzzling phenomena, such as the transmission of light waves and magnetic forces through a vacuum, until in the early twentieth century it was superseded by the development of quantum mechanics. This article is concerned only with the class of chemical compounds called ethers.

Represented structurally, the general formula for ethers is not unlike that of water or the alcohols:

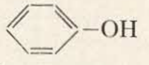
$H-O-H$	$R-O-H$	$R-O-R'$
water	alcohol	ether

(In organic chemical shorthand, the letters R and R′ indicate the presence of hydrocarbon groups.)

By replacing one of the hydrogen atoms in the water molecule with an alkyl group, an alcohol is obtained. If, instead, an aryl group replaced the hydrogen atom, a phenol (aromatic compound with hydroxyl group) would be produced. If both hydrogen atoms in the water molecule are replaced by hydrocarbon groups, the product is an ether. Additionally, if both hydrocarbon groups are identical the ether is called "symmetrical" in composition; if the groups differ, the ether is termed "asymmetrical." For example:

an alcohol $\left\{ CH_3-CH_2-OH \right.$
methyl alcohol

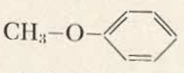
a phenol



phenol (carbolic acid)

a symmetrical ether $\left\{ \begin{array}{l} CH_3-CH_2-O \\ -CH_2-CH_3 \end{array} \right.$
diethyl ether

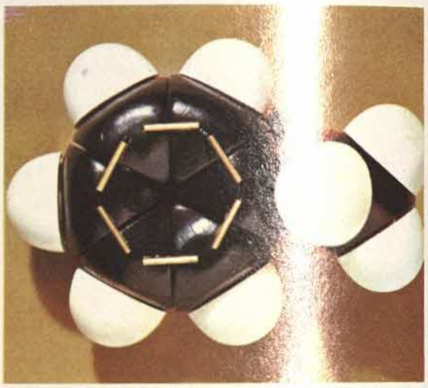
an asymmetrical ether



methyl phenyl ether

In these compounds, the bonds actually occur between the oxygen and carbon atoms; the formulas do not show the positions of the atoms in the molecules.

2



METHYL PHENYL ETHER—This illustration shows the molecular structure of an asymmetrical ether (an ether in which the hydrocarbon groups attached to the oxygen atom are different from one another). Asymmetrical ethers in general, and alkyl-aryl ethers in particular, can be manufactured by the Williamson process in which an alkyl halide is reacted with a sodium alcoholate or sodium phenate.

Ether compounds exhibit little reactivity because the C–O–C bonds are very stable (they are highly resistant to being broken). This property enhances their use as solvents for other organic substances and makes them well suited for use in the most delicate reactions where the presence of the solvent must have no effect on the formation of the products. Ethers approach alkanes in inertness. The alkoxy group is not damaged by most strong acids or bases and resists splitting

3

DIVINYL ETHER—While many ethers having a small number of carbon atoms in their molecules exhibit anesthetic properties, only divinyl and diethyl ether are used as anesthetics. All other ethers are either difficult to administer properly or have too high a degree of toxicity.

by oxidation or by a Grignard reagent. However, ethers are split fairly easily by concentrated halogen acids, particularly hydriodic acid, which reacts with, for example, methyl propyl ether, when moderately heated, to form propyl alcohol and methyl iodide on a molecule-for-molecule basis:

$$CH_3{-}O{-}CH_2{-}CH_2{-}CH_3 + HI \rightarrow CH_3{-}CH_2{-}CH_2{-}OH + CH_3I.$$

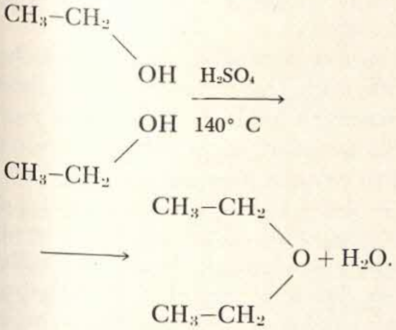
A common occurrence in organic reactions is that the products react in turn to form new, and possibly unwanted, compounds. In the previous example, an excess of hydriodic acid could continue to act on the propyl alcohol to form propyl iodide:

$$CH_3{-}CH_2{-}CH_2{-}OH + HI \rightarrow CH_3{-}CH_2{-}CH_2I + H_2O.$$

Thus, the organic chemist must use special techniques to determine where his reaction is going so that he obtains only the end products he seeks.

One characteristic of the aliphatic, or open chain ethers is a tendency to change into unstable peroxides on prolonged contact with air. These peroxides are highly explosive even in low concentrations, and consequently aliphatic ethers require great care in handling.

The most notable member of the ether series is diethyl ether. Because the oldest method of manufacture, still quite common, involves dehydrating ethyl alcohol with concentrated sulfuric acid, this compound has been called sulfuric ether (incorrectly, by present standards). The manufacturing process is quite straightforward:



Diethyl ether is a light, colorless, highly volatile liquid. It boils at only 35° C (95° F), and because its vapors form explosive mixtures with air, care must be exercised in handling the compound. However, the ease with which diethyl ether vaporizes makes it useful as an anesthetic inhalant. The action of the ether is on the central nervous system; hence it is a general, rather than a local, anesthetic. Prior to total relaxation, the patient experiences a sense of intoxication and may experience hallucinations. Ether taken internally is similar in effect to ingested alcohol.

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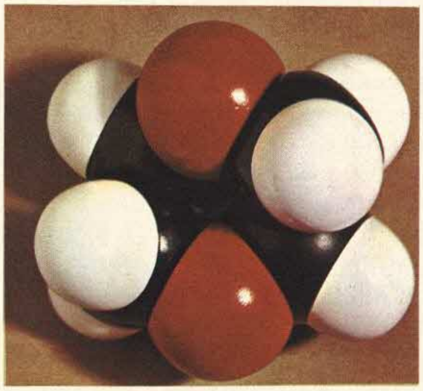


DIOXANE—Paralleling the "open-chain" ethers in manufacture and chemical behavior is the series of cyclic ethers. Structurally, these compounds belong to the heterocyclic series. One of the most interesting and important cyclic ethers is dioxane, which is used mainly as a solvent.

Other ethers with low molecular weights could also be used as general anesthetics, but for drawbacks such as a high degree of toxicity and difficulty of administration. Divinyl ether is sometimes used, but diethyl ether remains the compound of choice.

Another method used to prepare diethyl ether is to pass ethyl alcohol over a dehydrating agent such as magnesium sulfate or aluminum oxide, at high temperatures. Other ether compounds can be produced by these methods, but the reactions must be controlled carefully. For example, alcohols can be dehydrated, resulting in the formation of alkenes:

$$\underset{\text{ethyl alcohol}}{CH_3{-}CH_2{-}OH} \rightarrow \underset{\text{ethylene}}{CH_2 = CH_2} + H_2O.$$

Additionally, these methods can be used only when the products are to be symmetrical ethers. For instance, if two different alcohols react in the process, a mixture of three ethers is the result:

$$R{-}OH + R'{-}OH \rightarrow R{-}O{-}R' + H_2O;$$

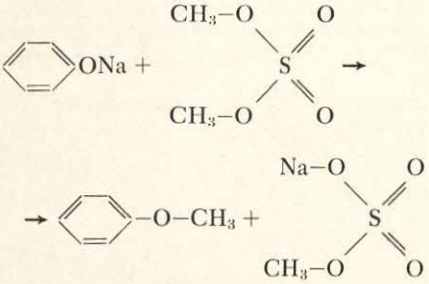
$$R{-}OH + R{-}OH \rightarrow R{-}O{-}R + H_2O;$$

$$R'{-}OH + R'{-}OH \rightarrow R'{-}O{-}R' + H_2O.$$

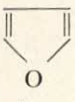
A method used to manufacture ethers of all types is the Williamson process, in which a sodium alcoholate or a sodium phenate is reacted with an alkyl halide:

$$R{-}ONa + R'{-}Br \rightarrow R{-}O{-}R' + NaBr.$$

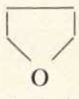
The Williamson process is a simple method to synthesize asymmetrical ethers, and finds special importance in the manufacture of the aromatic series. Given the stability of the aromatic halides, however, sodium phenates, rather than aryl halides, should be used in the reaction, which then proceeds with an alkyl halide. For methylation a dimethyl sulfate may be substituted for the halide:



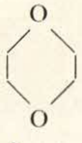
Compounds consisting of a ring formed by one or more oxygen and carbon atoms have a special place in the ether family, and are called cyclic ethers. The primary members of this group are furan, tetrahydrofuran, and dioxane:



furan



tetrahydrofuran



dioxane

Structurally, it is evident that these compounds belong to the heterocyclic series (where different types of atoms are joined in a ring). Their chemical behavior, however, parallels that of the ethers.

Furan is a compound in which a combination of double bonds and the possi-

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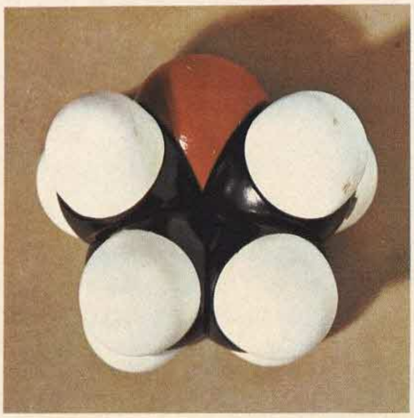
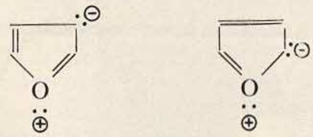


TETRAHYDROFURAN—This is the most important member of the cyclic ether series. Produced by hydrogenating furan, tetrahydrofuran has a wide range of industrial uses —as an intermediary in the synthesis of nylon and the manufacture of special aromatic compounds, and as a solvent in certain organic reactions between compounds that cannot be dissolved in ordinary ether.

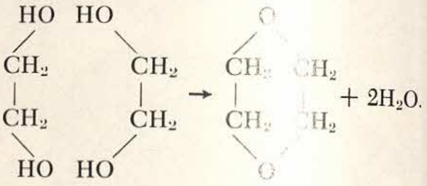
bility of dipolar forms results in considerable resonance stability (similar to the aromatic ring structure):



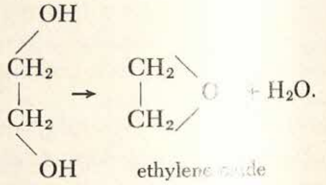
But, many of its reactions are typical of ethers.

Tetrahydrofuran, on the other hand, is a genuine ether. It is obtained by hydrogenating furan in the presence of a nickel catalyst. Tetrahydrofuran's ring can be opened by treatment with hydrochloric acid, thus giving the compound its importance in many chemical processes. The tetrahydrofuran molecule no longer has the aromatic properties associated with its precursor, furan. In scientific research, tetrahydrofuran is used as an efficient solvent, enabling delicate reactions to be conducted with substances insoluble in diethyl ether.

Dioxane also exhibits high solvent properties. It is produced by dehydrating ethylene glycol (a major component of "permanent" antifreeze):



Three-atom rings are usually less stable than six-atom rings because of distorted bond angles. For this reason, the dehydration occurs between hydroxyl groups of two separate molecules rather than between those of the same molecule. If dehydration occurred within the same molecule, a relatively unstable three-atom ring would be produced:



In actuality, ethylene oxide is produced commercially by methods such as the catalytic oxidation of ethylene in air. This oxide is the simplest member of the epoxy group—a group of cyclic ethers wherein the ring is formed by only three atoms. In a triatomic ring, the mean value of the bond angles is 60°, while the normal bond angle in the tetrahedral carbon atom is about 109°, and in bivalent oxygen at least 105°. Thus, the triatomic ring molecule is very reactive. A case in point is cyclopropane, which, though a saturated compound, has a reactivity comparable to unsaturated hydrocarbons.

Because the epoxy ring is easily broken with acids, bases, and other common reagents, it lends itself to use in many syntheses that might otherwise require more complex processes.

A well-known and useful product of polymerization of an epoxide is epoxy resin, used chiefly in coatings and adhesives. The most versatile of all adhesives, epoxy resins provide excellent adhesion to both porous and nonporous materials, including metals. Epoxies harden by chemical action.

CELLULOSE ACETATE SPINNING PLANT—Until recently, compounds produced by the elimination of water in an acid-alcohol reaction were called ethers. Showing properties quite different from true ethers, such compounds are now termed "esters." The illustration shows the spinning of cellulose acetate fibers into yarn.

Cellulose acetate, which at one time was considered an ether, is used in large quantities to manufacture rayon acetate, a synthetic fiber used in manufacturing textiles.

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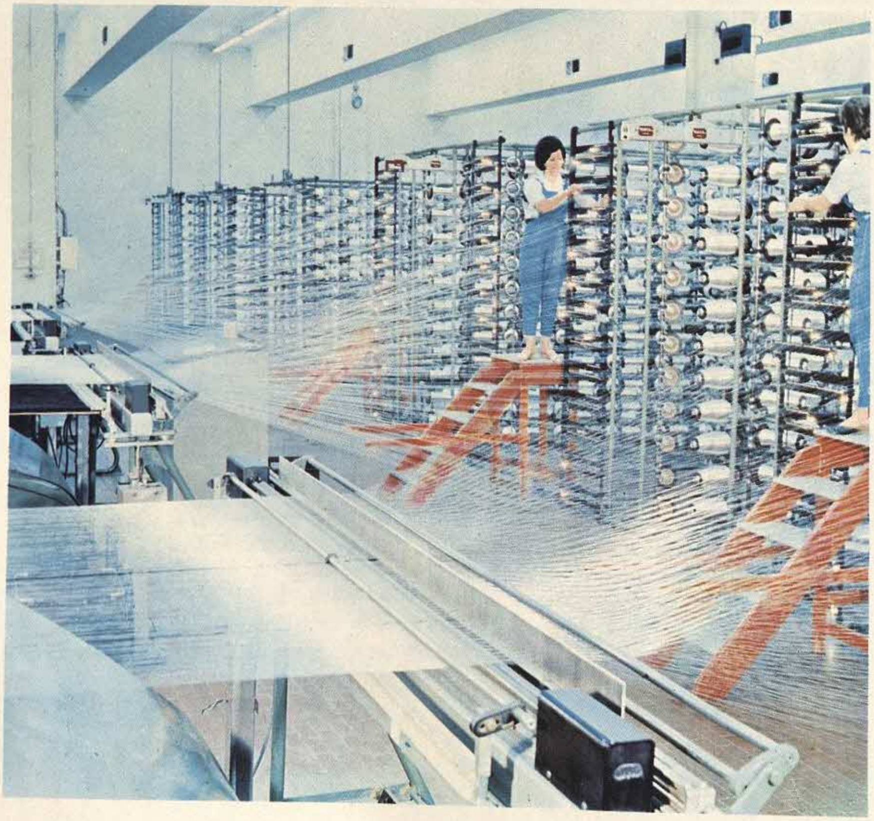
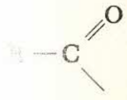


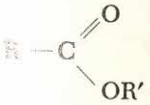
ESTERS | important derivatives of the carboxylic acids

The esters are extremely important functional derivatives of carboxylic acids. All of the functional derivatives of carboxylic acids are characterized by the acyl group:



$$R-C{\overset{O}{\diagup\!\!\diagup}}$$

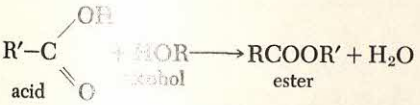
In the case of esters, the −OH group of the acid (RCOOH) is replaced by an −OR′ group:



$$R-C{\overset{\diagup\!\!\diagup O}{\underset{\diagdown OR'}{}}}$$

Esters may be considered the organic equivalent of inorganic salts. They are produced by the elimination of a water molecule from an acid and an alcohol:

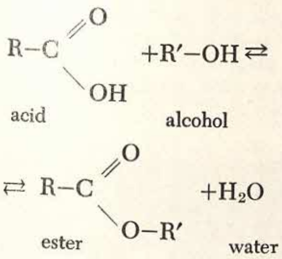
$$\underset{\text{base}}{XOH} + \underset{\text{acid}}{YH} \longrightarrow \underset{\text{inorganic salt}}{XY} + H_2O$$



$$\underset{\text{acid}}{R'-C{\overset{OH}{\underset{O}{}}}} + \underset{\text{alcohol}}{HOR} \longrightarrow \underset{\text{ester}}{RCOOR'} + H_2O$$

Despite their similarity to inorganic salts, esters are markedly organic substances. With the exception of the first few members of the series, they are sparingly soluble in water.

Esters are prepared by heating a carboxylic acid and an alcohol in the presence of a small quantity of a mineral acid that acts as a catalyst. In the expression



$$\underset{\text{acid}}{R-C{\overset{O}{\underset{OH}{}}}} + \underset{\text{alcohol}}{R'-OH} \rightleftarrows$$
$$\rightleftarrows \underset{\text{ester}}{R-C{\overset{O}{\underset{O-R'}{}}}} + \underset{\text{water}}{H_2O}$$

where R and R′ are any two organic radicals, the reversed arrows indicate that the reaction is at equilibrium; that is, the rate of the forward reaction equals the rate of the reverse reaction. Put another way, the ratio of the product of the concentrations of the reaction products to the product of the concentrations of the reactants is a constant K_c. In symbols,

$$K_c = [RCOOR'][H_2O] / [RCOOH][R'OH].$$

When a carboxylic acid is simply mixed with an alcohol, equilibrium is reached very slowly. It is, therefore, necessary to increase the speed of the reaction; this can be done by means of a catalyst. As mentioned, the most frequently used catalysts in esterification reactions are mineral acids (HCl, H_2SO_4) in extremely small quantities. For example, if acetic acid is reacted with ethanol in the absence of a catalyst, the reaction reaches equilibrium after several days. The addition of a small quantity of concentrated sulfuric acid or of hydrochloric acid, however, increases the rate of reaction so that equilibrium is reached within a few hours.

To shift the equilibrium in favor of the formation of the ester, it is also possible to eliminate the product water or to remove the ester as fast as it is being formed. Since the ratio shown above must remain constant, this leads to the formation of further products.

If the esterification reaction does not take place rapidly enough after a catalyst has been added, the ester can be prepared as follows:

$$R'COOAg + XR \longrightarrow R'COOR + AgX.$$

R′COOAg is the silver salt of an organic acid, and XR is an alkyl halide, such as ethyl bromide, C_2H_5Br. This method, however, involves considerable expense.

Other reactions are frequently used to prepare esters. Two of these are:

$$\underset{\text{anhydride}}{(RCO)_2O} + \underset{\text{alcohol}}{R'OH} \longrightarrow \underset{\text{ester}}{RCOOR'} + \underset{\text{acid}}{RCOOH}$$

and

$$\underset{\text{acid chloride}}{RCOCl} + \underset{\text{alcohol}}{R'OH} \longrightarrow \underset{\text{ester}}{RCOOR'} + \underset{\text{hydrogen chloride}}{HCl}$$

where R′, in both cases, can be either an alkyl or an aryl radical (CH_3- or C_6H_5-, for example). Two additional methods are as follows:

$$\underset{\text{amide}}{RCONH_2} + \underset{\text{alcohol}}{R'OH} \longrightarrow \underset{\text{ester}}{RCOOR'} + \underset{\text{ammonia}}{NH_3}$$

and

$$\underset{\text{nitrile}}{RC{\equiv}N} + \underset{\text{alcohol}}{R'OH} + \underset{\text{water}}{H_2O} \longrightarrow \underset{\text{ester}}{RCOOR'} + \underset{\text{ammonia}}{NH_3}$$

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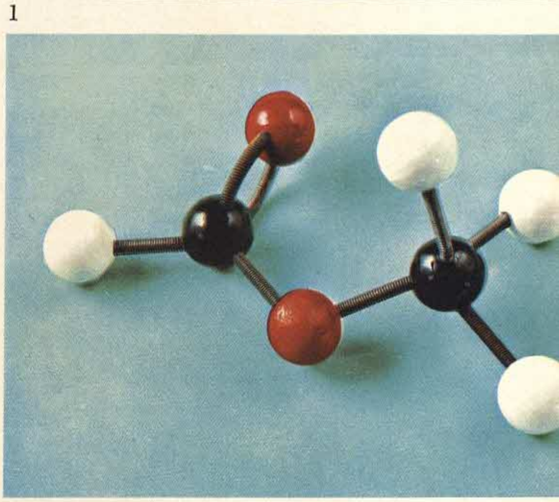


METHYL FORMATE—Esters of the lower fatty acids with saturated alcohols are volatile liquids with a pleasant odor. Higher members of the series are solids with almost no odor.

Methyl formate ($HCOOCH_3$) has a melting point of −100° C (−148° F), a boiling point of 32° C (89.6° F), and a density lower than the density of water.

The illustration shows a molecular model of $HCOOCH_3$. The white spheres represent hydrogen, the black carbon, and the red oxygen.

The choice of a method depends on the availability of reagents. For example, one method that calls for special care is the following:

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2.$$

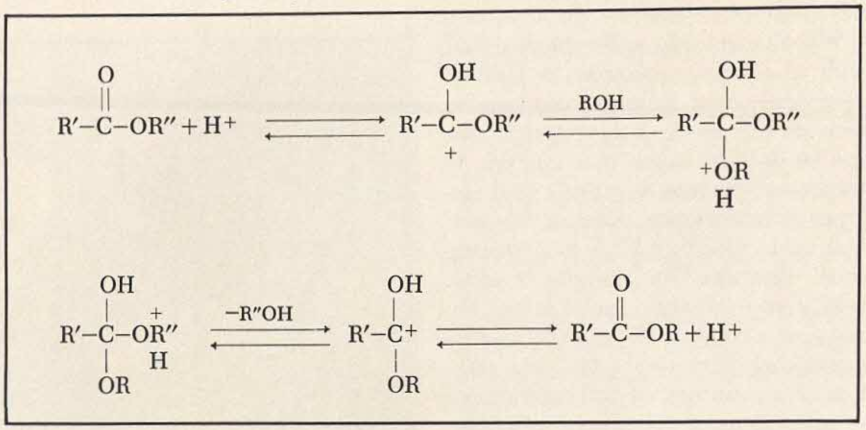
In this case, the reagent is explosive and poisonous.

Another extremely important reaction for the preparation of esters is so-called transesterification. This method involves the base catalyzed reaction of an alcohol with an ester to produce a new ester plus the alcohol of the first ester.

Transesterification is a reversible process; however, by forcing the equilibrium toward the end product by means of an excess of the alcohol employed in the interchange, satisfactory yields can be obtained. The transesterification reaction is catalyzed by both acids and bases according to two different mechanisms, as follows:

$$R'COOR'' + ROH \xrightleftharpoons{H^+ + OH^-} R'COOR + R''OH.$$

One possible mechanism of a transesterification reaction catalyzed by an acid is as follows:



$$R'-\overset{\overset{\displaystyle O}{\|}}{C}-OR'' + H^+ \rightleftharpoons R'-\underset{+}{\overset{\overset{\displaystyle OH}{|}}{C}}-OR'' \xrightleftharpoons{ROH} R'-\underset{\underset{\displaystyle \overset{+}{O}R\atop H}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-OR''$$

$$R'-\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}-\underset{H}{\overset{+}{O}}R'' \xrightleftharpoons{-R''OH} R'-\underset{\underset{\displaystyle OR}{|}}{\overset{\overset{\displaystyle OH}{|}}{C}}{}^+ \rightleftharpoons R'-\overset{\overset{\displaystyle O}{\|}}{C}-OR + H^+$$

With regard to the acid reagents, it may be useful to know that the longer the hydrocarbon chain, the slower the reaction. The reactivity of alcohols, however, depends on the location of the $-OH$ group within the molecule. Primary alcohols react more rapidly than secondary alcohols, and secondary more rapidly than tertiary alcohols.

PHYSICAL PROPERTIES OF ESTERS

Esters are generally liquids; only those with a high molecular weight are solids. Esters are practically insoluble in water; they are, however, soluble in both alcohol and ether.

Although they have higher molecular weights than the acids from which they are derived, esters have lower boiling points because there are no hydrogen bonds between molecules, as in organic acids.

Esters derived from solid acids, in turn, have lower fusion (melting) points than the corresponding acids. They are also more soluble in organic solvents. Esters have a pleasant smell. Indeed, the scent of many flowers and fruits is due to a mixture of volatile esters. This is also true of many artificial aromas.

CHEMICAL PROPERTIES

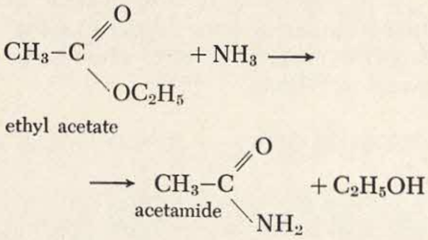
An acid and an alcohol are produced from an ester by means of hydrolysis. Such reactions can be carried out in the presence of acidic or basic catalysts. The reduction of an ester, on the other hand, leads to two alcohols:

$$RCOOR' + 2H_2 \xrightarrow{\text{catalyst}} RCH_2OH + R'OH$$

or

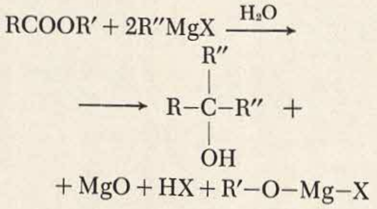
$$RCOOR' \xrightarrow[\text{in alcohol}]{\text{sodium}} RCH_2OH + R'OH$$

If an ester is treated with ammonia (NH_3) in an alcohol solution, an amide is produced. For example:



$$CH_3-C(=O)OC_2H_5 + NH_3 \longrightarrow CH_3-C(=O)NH_2 + C_2H_5OH$$

Moreover, esters react with Grignard reagents to yield tertiary alcohols:

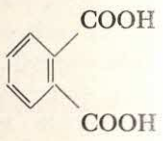


$$RCOOR' + 2R''MgX \xrightarrow{H_2O} R-\underset{\underset{\displaystyle OH}{|}}{\overset{\overset{\displaystyle R''}{|}}{C}}-R'' + MgO + HX + R'-O-Mg-X$$

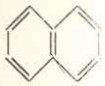
SOME IMPORTANT ESTERS

Esters are one of the most important substances of the chemical industry. Soaps, waxes, synthetic textile fibers, cosmetics, perfumes, pharmaceuticals (particularly aspirin), solvents for paints and plastics, artificial food flavors, plasticizers—these are only a few of the great number of products in which esters play a significant part. Some esters of great industrial interest are as follows:

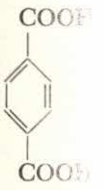
The esters of phthalic acid



produced by oxidation of naphthalene

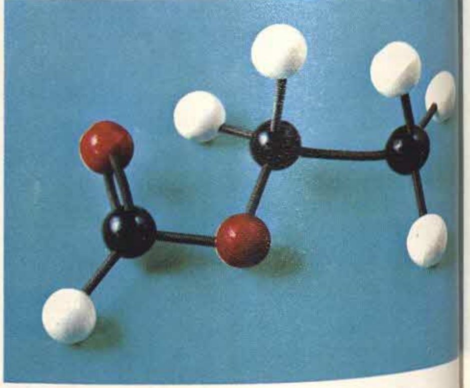


are of fundamental importance in various industrial areas, including textiles, synthetic resins, paints, and plastic linings. In the field of synthetic fibers an isomer of phthalic acid rather than the acid itself is used. The isomer in question is terephthalic acid, a compound in which the substituted groups are identical but situated in different positions:



Phthalates can be used as plasticizers; that is, they serve to make some polymers more flexible when they are too fragile in their natural state.

Phthalates serve this function either by bonding with the chains of the polymer, thus producing a network structure, or by being inserted between the chains and



ETHYL FORMATE—Ethyl formate, $HCOOC_2H_5$, just as methyl formate, boils at a temperature lower than the boiling point of either the acid or the alcohol from which it is derived; its boiling point is 54° C (129.2° F).

Ethyl formate freezes at $-80°$ C ($-112°$ F); its density at 20° C (68° F) is 0.906 grams/cm^3.

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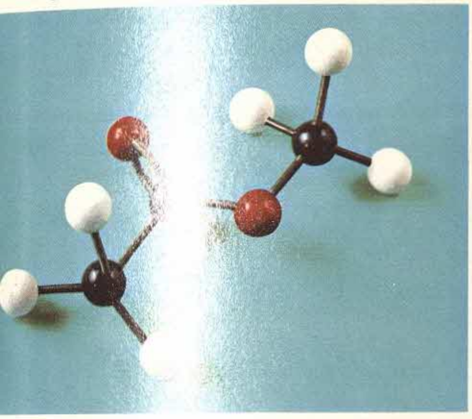

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METHYL ACETATE—The methyl and ethyl esters are liquids. There are no hydrogen bonds in these liquids. Hence, they boil at lower temperatures than the corresponding acids (which contain hydrogen bonds) despite the fact that they have higher molecular weights.

Methyl acetate, CH_3COOCH_3, freezes at −98° C (−144° F) and boils at 57° C (134.6° F); its density at 20° C (68° F) is 0.934 g/cm³.

acting as an external plasticizer. The disadvantage of this is that the phthalate slowly but steadily volatilizes. The product thus tends to become fragile with the passage of time.

The most frequently used phthalates are the propyl, butyl, isobutyl, isoamyl, allyl, and hexyl.

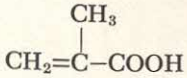
Esters are useful not only to modern synthetic chemistry. Waxes, for example, are esters of the higher fatty acids (acids with a long hydrocarbon chain) and of the higher alcohols.

Fats and oils are also esters. In these cases the alcohol is a polyhydric alcohol; that is, an alcohol with more than one −OH group; the glycerides (the fats and the oils that derive from polyhydric alcohols are generally called triglycerides). The acid part consists of acids with long hydrocarbon chains (fatty acids). Ordinary olive oil, for example, is the triglyceride of oleic acid.

Returning to plastic materials, the esters of acrylic and methacrylic acids are of some interest:

$$CH_2{=}CH{-}COOH$$

and

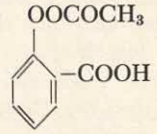


$$CH_2{=}\overset{\displaystyle CH_3}{\overset{|}{C}}{-}COOH$$

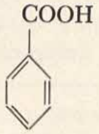
These esters polymerize and yield the widely used acrylic resins. The esters of acrylic acid are also used in artificial textile fibers.

Rayon is yet another ester (the alcohol part is made up of cellulose). An ester known as bis-2,ethyl-hexyl-sebacate is used in jet turbines.

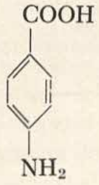
Among the esters used in the pharmaceutical field, the most famous is undoubtedly common aspirin, the sodium salt of the ester-acid, acetylsalicylic acid:



The derivatives of benzoic acid



and para-amino-benzoic acid



are also widely used as cardiotonics, anesthetics, and fungicides.

Esters also find many applications in the cosmetics and perfume industries. The most common fruit odors are due to esters; amyl acetate has a pear-like odor, and amyl butyrate gives the apricot its characteristic scent.

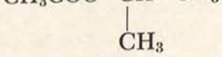
From a quantitative point of view, esters find their greatest application as solvents in the paint and plastics industries. Some examples are:

$$CH_3COOCH_3$$

methyl acetate

$$CH_3COOCH_2CH_3$$

ethyl acetate



$$CH_3COO{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}CH_3$$

isopropyl acetate

$$CH_3COOCH_2CH_2CH_2CH_3$$

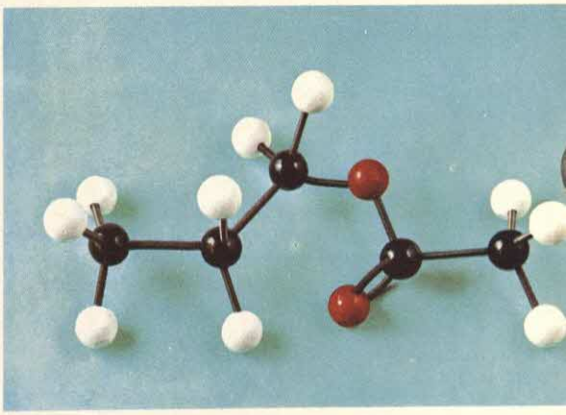
butyl acetate

$$CH_3COOCH_2CH_2CH_2CH_2CH_3$$

amyl acetate

ESTERS OF INORGANIC ACIDS

The esters of inorganic acids constitute a class of their own. These compounds are formed by means of reaction between inorganic acids and alcohols. The sulfates are widely used as intermediates in the chemical industry (methyl sulfate, CH_3OSO_3H, for example) and as detergents (sulfates of higher alcohols such as the sodium salt of lauryl sulfate, $C_{11}H_{23}CH_2OSO_3^{-}Na^{+}$). Organic nitrates are associated with the name of Alfred Nobel, the Swedish inventor who introduced the industrial production of nitrocellulose (obtained by treating cellulose with a mixture of nitric and sulfuric acids). Nitrocellulose lacquers are used to spray-coat automobiles, airplanes, and furniture and to dip-coat hardware, brush handles, and other mass-produced items. Lacquer coatings that contain nitrocellulose improve the oil resistance and washability of paper. Nitrocellulose plastics are widely used in eyeglass frames. Artificial leather is made by coating cotton fabrics with solutions containing nitrocellulose. Among the phosphates, certain derivatives of pyrophosphoric acid are used as insecticides.



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N-PROPYL ACETATE—Esters are used in the purification of the corresponding acids and for the separation of several different acids.

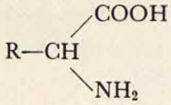
$CH_3COOC_3H_7$ is the formula for n-propyl acetate. It is a liquid at ordinary temperatures. It freezes at −92° C (−133.6° F) and boils at 101.7° C (about 214° F). Its density is lower than the density of water—0.886 g/cm³ at a temperature of 20° C (68° F).

THE AMINO ACIDS | the first chapter in the chemistry of life

Proteins are the fundamental constituents of every living cell, whether it is animal or plant. These proteins are made by the condensation of various molecules of amino acids. The very origin of life on Earth may well have come about by the initial formation of amino acids in the primeval waters, subsequently condensed into protein substances. The human body is about 16 percent amino acids by weight; about half of the organic materials contained in the human body are amino acids. In addition, protein chains contribute to the buildup of various active substances essential to living organisms, such as enzymes—the catalysts of metabolic reactions.

Amino acids are characterized by the presence of the carboxyl group ($-COOH$) and amine group ($-NH_2$) in the same molecule. Their properties derive from the coexistence of these two groups of opposite nature—the first is an acid; the second, a base.

The α-amino acids are particularly interesting from the physiological and practical point of view. In them, the carboxyl and amine groups are bound to the same carbon atom, as shown below.



$$R{-}CH\begin{matrix} ^{\diagup COOH} \\ _{\diagdown NH_2} \end{matrix}$$

The R-group can be a hydrocarbon chain, or it can include other functional groups (even other amine and carboxyl groups). Amino acids containing more amine than acid groups are called basic amino acids; those containing more carboxyl groups than amine groups are referred to as acids. Lysine is an example of the former, and aspartic acid and glutamic acid are examples of the latter.

GLYCINE—This was the first amino acid to be obtained and isolated by hydrolysis of proteins. It constitutes 10 percent of the protein part of an animal organism.

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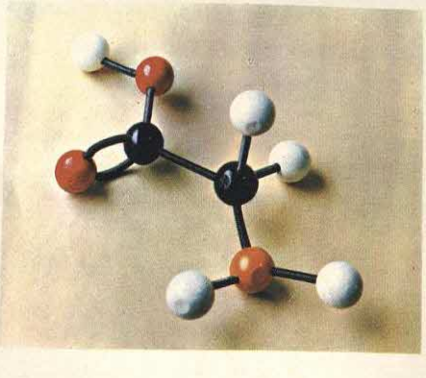
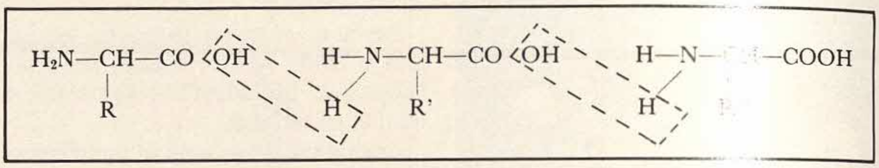


Protein chains consist of long sequences of amino acids with the linkage $-CO-NH-$. This linkage could be the result of a polymerization condensation reaction between opposite polar groups with elimination of water.

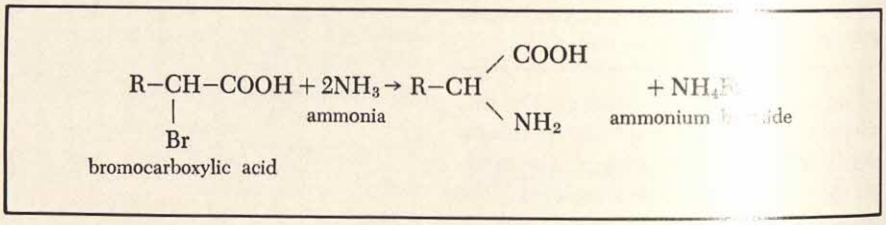


Proteins can be classified by the length of their polyamide chains (which can reach several thousand units), by the type of constituent amino acids, and by the sequence in which the amino acids are bound together.

The amino acid content of proteins varies considerably. Glycine (H_2N-CH_2-COOH) is lacking in albumin, but is relatively rich in gelatin. The keratines (proteins in hair and epidermal tissue) are rich in cystine, an amino acid that contains sulfur. Polypeptides can be obtained by the degradation of proteins, although they are also found in nature. Polypeptides have a structure analogous to that of protein; they are, however, constituted of short sequences of amino acids.

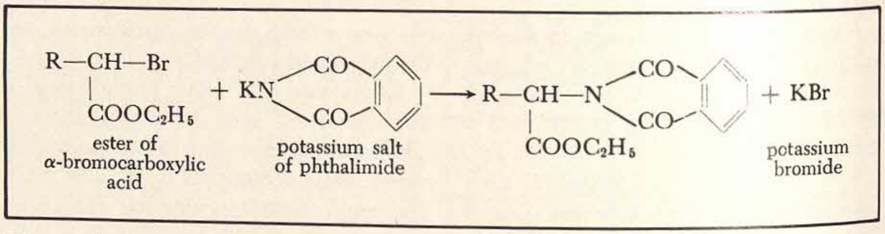
PREPARATION OF THE α-AMINO ACIDS

A classic method for synthesizing the α-amino acids is the reaction of the halogenated carboxylic acids with ammonia:

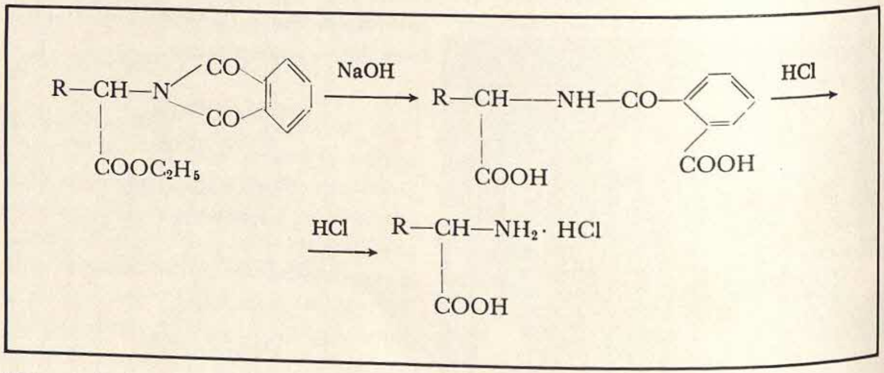


$$\underset{\text{bromocarboxylic acid}}{\underset{|\atop Br}{R-CH}-COOH} + \underset{\text{ammonia}}{2NH_3} \rightarrow R-CH\begin{matrix} ^{\diagup COOH} \\ _{\diagdown NH_2} \end{matrix} + \underset{\text{ammonium}}{NH_4}$$

The reaction between the esters of the halogenated acids and the potassium salt of phthalimide can be considered a modification of this synthesis.

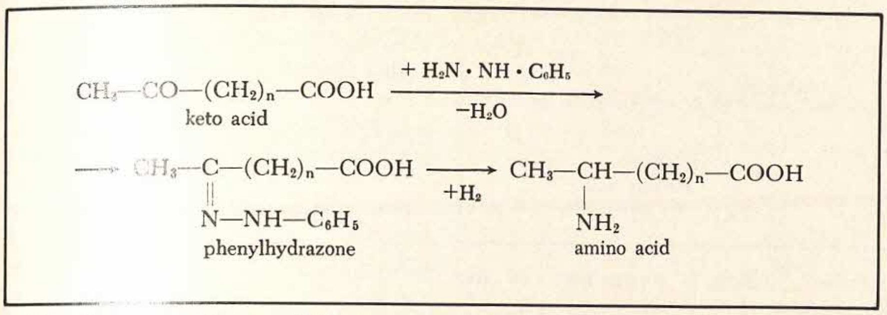


The product is hydrolyzed, first with sodium hydroxide, and then with hydrochloric acid, as represented by the following structure:



This results in an amine salt. Treating the amine salt with an alkaline solution yields the amino acid again.

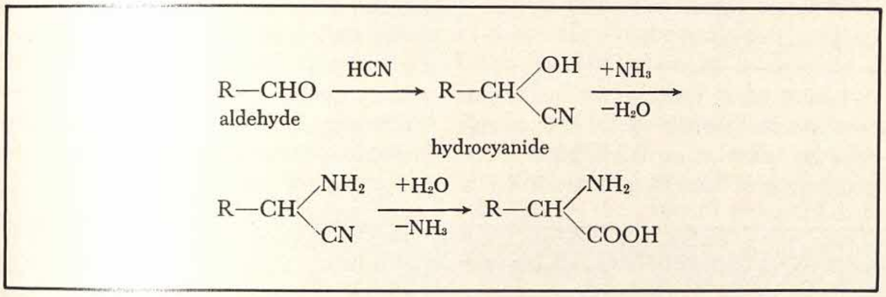
Amino acids can also be prepared from another category of bifunctional compounds—the keto acids—that contain the carbonyl group ($\geq C=O$) in addition to the carboxyl group. In the first stage of preparation the keto acid reacts with phenylhydrazine to form the corresponding phenylhydrazone with the elimination of water. The phenylhydrazone is then reduced with activated hydrogen, as shown by the following:



$$\underset{\text{keto acid}}{CH_3{-}CO{-}(CH_2)_n{-}COOH} \xrightarrow[-H_2O]{+H_2N\cdot NH\cdot C_6H_5}$$

$$\longrightarrow \underset{\text{phenylhydrazone}}{CH_3{-}\underset{\underset{N-NH-C_6H_5}{\|}}{C}{-}(CH_2)_n{-}COOH} \xrightarrow{+H_2} \underset{\text{amino acid}}{CH_3{-}\underset{\underset{NH_2}{|}}{CH}{-}(CH_2)_n{-}COOH}$$

The Strecker synthesis, which is more commonly used in laboratory preparations, consists of the addition of prussic acid to the carbonyl group of an aldehyde. This forms a hydrocyanide, whose hydroxyl group is converted to an amine with ammonia. The $-CN$ group is then saponified by an acid treatment.

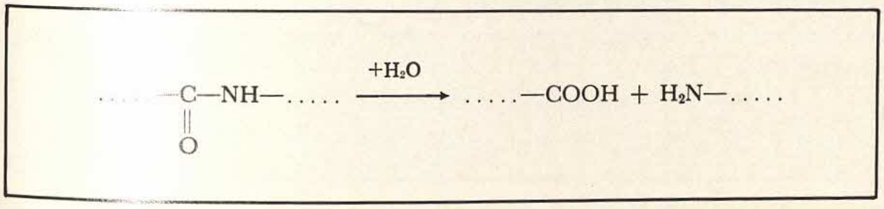


$$\underset{\text{aldehyde}}{R{-}CHO} \xrightarrow{HCN} \underset{\text{hydrocyanide}}{R{-}CH\begin{matrix}OH\\CN\end{matrix}} \xrightarrow[-H_2O]{+NH_3}$$

$$R{-}CH\begin{matrix}NH_2\\CN\end{matrix} \xrightarrow[-NH_3]{+H_2O} R{-}CH\begin{matrix}NH_2\\COOH\end{matrix}$$

The synthesis is carried out rapidly and easily by using commercially available salts: ammonium chloride (NH_4Cl) and sodium cyanide ($NaCN$).

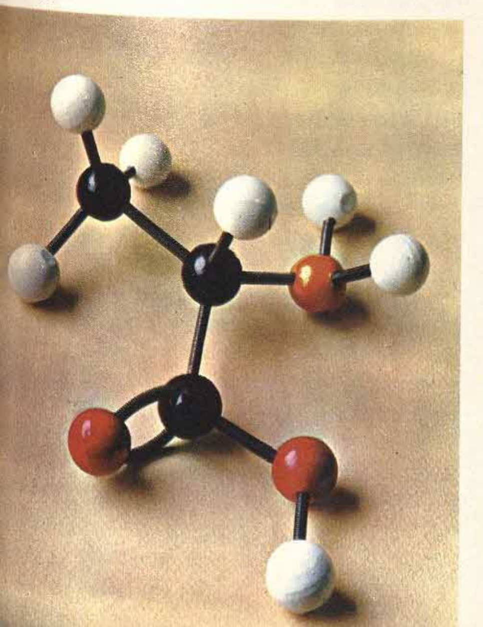
The main sources of α-amino acids are the natural proteins, such as albumin. Proteins are broken down by methods that are of great practical interest. The amide bonds are hydrolyzed by special fermenting agents (such as pepsin or trypsin), or by treatment with heat and dilute sulfuric or hydrochloric acid. The acid and base functional groups of the amino acids are thus reobtained.



$$\ldots\ldots{-}\underset{\underset{O}{\|}}{C}{-}NH{-}\ldots\ldots \xrightarrow{+H_2O} \ldots\ldots{-}COOH + H_2N{-}\ldots\ldots$$

ALANINE—The dextrorotatory form of this amino acid occurs in nature. It was the first amino acid to be synthesized, using the Strecker method. This synthesis can be done readily with commercially available salts.

2



The enzymes pepsin and trypsin also act on food proteins during digestion. Pepsin is most active in a weak acid solution; trypsin, in a slightly alkaline environment. Moreover, pepsin does not degrade natural albumins beyond the polypeptide stage, while trypsin produces complete hydrolysis to amino acids.

The end products of these degradation reactions are complex mixtures of α-amino acids. Separating them out is a difficult problem. The monoaminodicarboxylic acids—such as aspartic acid and glutamic acid—can be separated due to the low solubility of their calcium and barium salts in aqueous alcohol. The basic amino acids can be precipitated from solutions with phosphotungstic (phosphowolframic) acid. Finally, the monoamino acids and monocarboxylic acids differ from the others in that they can be extracted from neutral solutions by the addition of butyl alcohol. Individual members of the monoaminodicarboxylic acids and basic amino acids can be extracted by means of selective precipitation of the salts formed with acids and bases. The problem is more difficult with monoamino acids and monocarboxylic acids. A method proposed by the German organic chemist Emil Fischer is to transform these substances into the corresponding ethyl esters (which are liquids that can be distilled) and then to separate them by fractional distillation. Other methods of preparation for specific amino acids are discussed further in subsequent paragraphs.

The synthesis of α-amino acids in living organisms is a problem of great biological interest. By 1970, the problem of how the living cell synthesizes protein had been all but completely clarified. Many laboratories had synthesized specific proteins. It is believed that the in-

3

THE SYNTHESIS OF AMINO ACIDS — The illustration shows a pilot plant for the synthesis of amino acids. This equipment, by allowing a single product to be synthesized, eliminates the problem of separation.

PROTEIN HYDROLYSIS—Shown in the photograph is a group of enameled reactors used for acid hydrolysis. The hydrolysis of proteins is the most important method for industrial production of amino acids.

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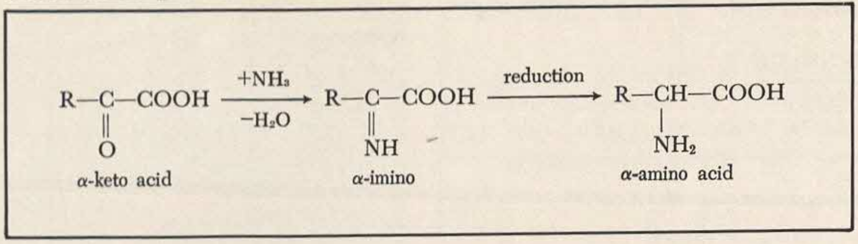
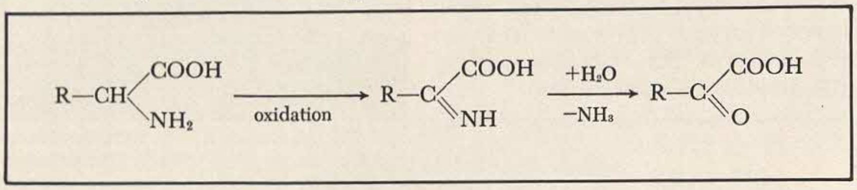
termediate compounds are α-keto acids and α-aminos.



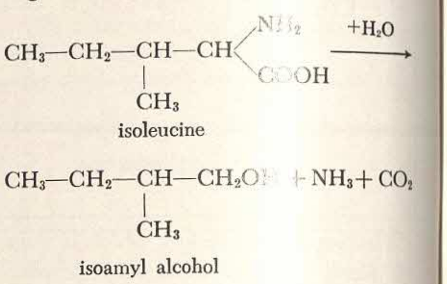
$$R{-}\underset{\underset{O}{\|}}{C}{-}COOH \xrightarrow[-H_2O]{+NH_3} R{-}\underset{\underset{NH}{\|}}{C}{-}COOH \xrightarrow{\text{reduction}} R{-}\underset{\underset{NH_2}{|}}{CH}{-}COOH$$

The biological degradation of amino acids is thought to follow the opposite reaction, which is represented by the structure:



Living organisms differ considerably from one another in their capacity to synthesize amino acids. The human body, for example, cannot synthesize eight of the amino acids required for making its own proteins; these essential amino acids must be taken in as nourishment if the organism is to have the proteins it needs.

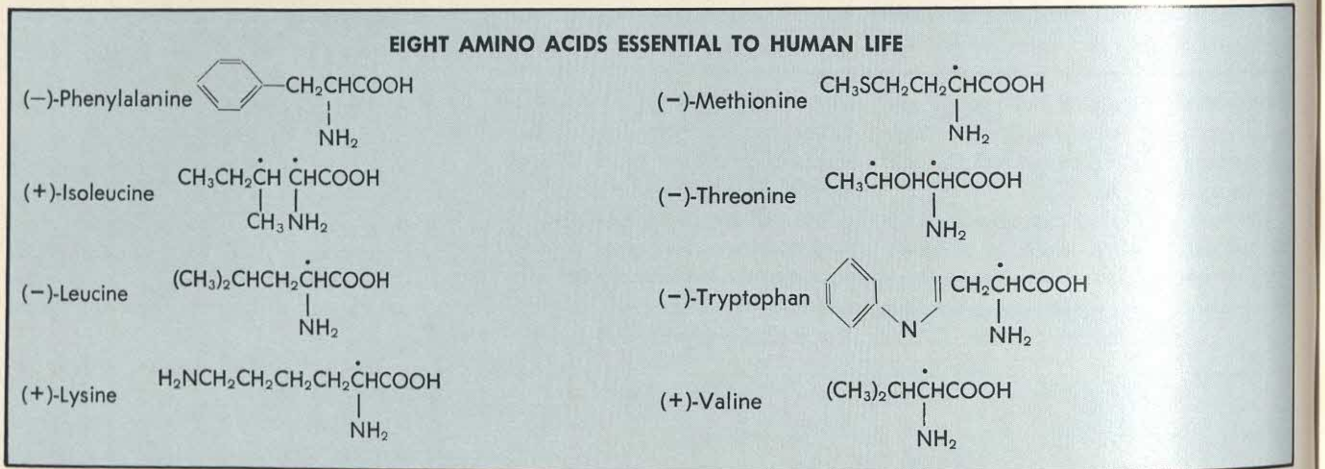
Alcohols are a product of some α-amino acid degradations. Fermentation produced by yeast can yield some of the higher alcohols.



$$CH_3{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH\langle^{NH_2}_{COOH} \xrightarrow{+H_2O} CH_3{-}CH_2{-}\underset{\underset{CH_3}{|}}{CH}{-}CH_2OH + NH_3 + CO_2$$

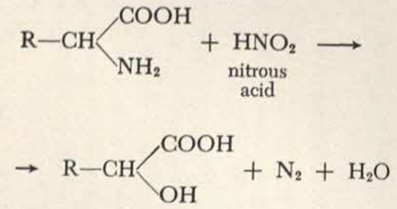
The α-amino acids are crystalline solids generally soluble in water and insoluble in anhydrous alcohols. Only two amino acids of protein origin—proline and hydroxyproline—are soluble in alcohol; these also have peculiar structures because they are the only ones among the natural α-amino acids that contain a secondary amine group.

EIGHT AMINO ACIDS ESSENTIAL TO HUMAN LIFE



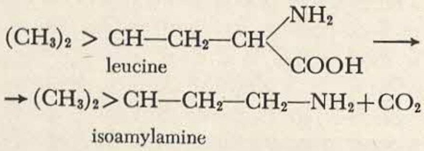
REACTIONS AND PROPERTIES OF THE α-AMINO ACIDS

Under suitable conditions α-amino acids undergo reactions characteristic of the primary amines. Particularly interesting is the transformation of amino acids into oxyacids by reaction with nitrous oxide, which liberates nitrogen.



$$R{-}CH\langle^{COOH}_{NH_2} + HNO_2 \longrightarrow R{-}CH\langle^{COOH}_{OH} + N_2 + H_2O$$

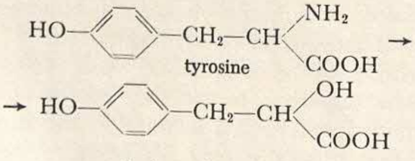
The foregoing reaction forms the basis of an analytic method for the quantitative determination of the primary amine groups in the amino acids. The α-amino acids can be made into amines by heating the acids in an inert solvent. Such a solvent serves the very valuable purpose of eliminating every trace of carbon dioxide present.



$$(CH_3)_2 > CH{-}CH_2{-}CH\langle^{NH_2}_{COOH} \longrightarrow (CH_3)_2 > CH{-}CH_2{-}CH_2{-}NH_2 + CO_2$$

This reaction can also be brought about by bacteria (*Bacillus proteus, B. coli,* or *B. subtilis*). These bacteria are responsible for formation of the toxic amines cadaverine, $NH_2{-}(CH_2)_5{-}NH_2$, and putrescine, $NH_2{-}(CH_2)_4{-}NH_2$, in the putrefaction of proteins, by decarboxylating the amino acids lysine and ornithine.

These reactions require an acid environment or they lead to the formation of oxyacids.



para-hydroxyphenyl lactic acid

Aqueous solutions of amino acids that contain a single $-NH_2$ group and a single $-COOH$ group are neutral, because the acidic and basic functional groups neutralize each other. This leads to the formation of a bipolar ion or zwitterion (a complex ion that is both positively and negatively charged). Glycine, for example, has the equilibrium in solution shown at the top of p. 95.

The dipolar ion corresponds to a true internal salt. In its formation, the amine group (due to its basic nature) acts as an acceptor of the H^+ proton generated by the acid dissociation of the carboxylic group.

Other kinds of ions can exist in aqueous solution at low and high pH values, due to the presence of—respectively—other acids and bases. Again using glycine as an example, in a high concentration of H^+ ions the carboxyl dissociation is reversed and the following ion results:

$$H_3\overset{+}{N}{-}CH_2{-}COOH$$

$$H_2N{-}CH_2{-}COOH \rightleftarrows H_3\overset{+}{N}{-}CH_2{-}COO^-$$

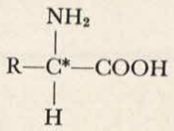
neutral glycine — dipolar ion

This corresponds to the protonation of the single $-NH_2$ group by the acid present in the solution.

In another case, the ion $H_2N{-}CH_2{-}COO^-$ is formed; this corresponds to the formation of a salt by the carboxyl group of the amino acid and the base present in the high solution.

Another important characteristic of α-amino acids is optical activity. An organic compound is optically active if it causes a rotation of the plane of polarization of plane polarized light passing through it. (Such optical activity is not restricted to crystalline solids.) In general, a compound is optically active if it has such a structure that it cannot be superimposed on its mirror image. This happens if the molecule contains an asymmetric carbon atom—a carbon atom with four different substituents.

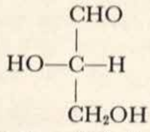
In the following general example, the asymmetrical carbon atom is identified with an asterisk:



$$R{-}\overset{\displaystyle NH_2}{\underset{\displaystyle H}{C^*}}{-}COOH$$

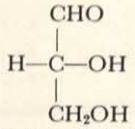
Glycine, the simplest amino acid, is not optically active: $H_2N{-}CH_2{-}COOH$. An optically active substance exists in the form of two isomers (called enantiomorphs) having identical chemical and physical properties except that they rotate the plane of the plane-polarized light through identical angles in opposite directions. The enantiomorphs correspond to the two mirror images that cannot be superimposed.

Depending on the direction in which they rotate the plane of polarized light, the isomers are called dextrorotatory (right-turning) or levorotatory (left-turning). This is indicated by the signs + or − before the amino acid and D or L before enantiomorphs, respectively. Glyceraldehyde and alanine are written as follows.



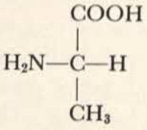
$$\begin{array}{c} CHO \\ | \\ HO{-}C{-}H \\ | \\ CH_2OH \end{array}$$

L-glyceraldehyde



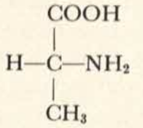
$$\begin{array}{c} CHO \\ | \\ H{-}C{-}OH \\ | \\ CH_2OH \end{array}$$

D-glyceraldehyde



$$\begin{array}{c} COOH \\ | \\ H_2N{-}C{-}H \\ | \\ CH_3 \end{array}$$

L-alanine



$$\begin{array}{c} COOH \\ | \\ H{-}C{-}NH_2 \\ | \\ CH_3 \end{array}$$

D-alanine

An α-amino acid prepared by normal means of laboratory synthesis from optically inactive products displays no optical activity.

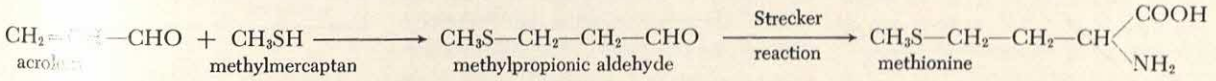
GLYCINE

Glycine, the first in the series of α-amino acids, is specially important because of its connection with the natural product known as betaine. Betaine is a dipolar form of glycine and has the character of an internal salt.

METHIONINE

This amino acid—of which only the D form is found in nature—contains a sulfur atom. It is used in medicine for the treatment of certain liver infections. In methionine the D and L forms are equally active biologically, and the racemic mixture obtained in synthesis can be used equally well.

The synthesis of this amino acid is according to the following reaction:



GLUTAMIC ACID

The monosodium salt of the L isomer of this acid is widely used as an additive to foodstuffs, to enhance the natural flavors and aromas. The hydrolysis of low-cost vegetable proteins is one of the important industrial preparations of glutamic acid. This reaction is generally carried out in aqueous solutions of hydrochloric acid at 110° C (230° F). It is completed in about 20 hrs.

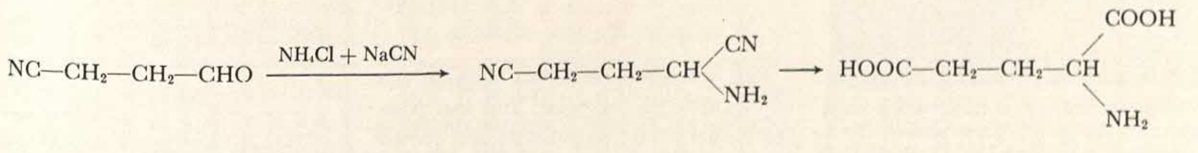
The hydrochloride of L-glutamic acid crystallizes easily from the final acid solution (after appropriate concentration) and is thus separated from other amino acids in solution.

Fermentation synthesis of glutamic acid—using suitable microorganisms—has become increasingly important in recent times. The raw materials are glucose (obtained from the amide by means of acid or enzyme hydrolysis) and a source of nitrogen (urea, ammonia, or ammonia salts).

A third method of industrial preparation, completely synthetic, uses acrylonitrile ($CH_2{=}CHCN$) as a raw material. This compound is first converted into β-cyanopropionic aldehyde. This reaction uses a cobalt-based catalyst and requires heat and pressure.

$$NC{-}CH{=}CH_2 + CO + H_2$$
$$\rightarrow \underset{\text{β-cyanopropionaldehyde}}{NC{-}CH_2{-}CH_2{-}CHO}$$

The racemic acid mixture is then obtained by the Strecker synthesis and saponification of the −CN groups.

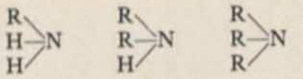


The importance of this synthesis is that acrylonitrile, the main raw material, can be obtained on a large scale, and at a low cost, from acetylene or ethylene. Unlike the first two processes, which employ natural raw materials and therefore yield the levorotatory isomer of glutamic acid, the method just described yields two optical isomers in equal parts. They are separated by a special process of crystallization and subsequent conversion of the dextrorotatory isomer.

ALIPHATIC AMINES | preparation and characteristic reactions

The amines occupy an important place among the organic derivatives of nitrogen. This is so because of the many chemical transformations that amines undergo. These compounds are used on a vast scale in industry, both as amines in the true sense and as starting materials for organic syntheses. Various substances of this class of compounds are of considerable physiological importance. They serve as regulators and stimulators of fundamental bodily functions.

Amines are derived from ammonia (NH_3) by substituting hydrocarbon radicals for one, two, or even three of the hydrogen atoms in the ammonia molecule. The classification of amines is thus based on the number of hydrocarbon radicals bonded to the nitrogen atom

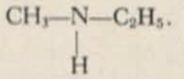


primary amine secondary amine tertiary amine

The characteristic amine groups are therefore as follows:

$-NH_2$: primary amine group
$>NH$: secondary amine group
$>N$: tertiary amine group

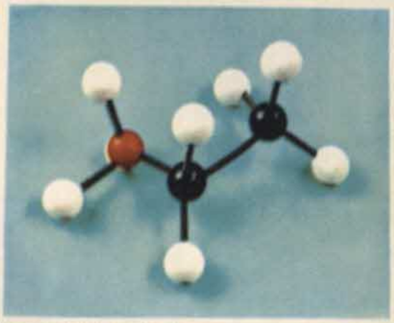
The substituting hydrocarbon radicals (aliphatic, alicyclic, aromatic, and so on) can all be of the same type, as in dimethylamine $(CH_3)_2NH$, or they can all be different, as in methylethylamine,



$$\underset{\displaystyle H}{\underset{|}{CH_3{-}N{-}C_2H_5.}}$$

These possibilities indicate how vast this class of nitrogen compounds is.

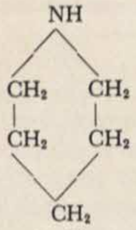
1



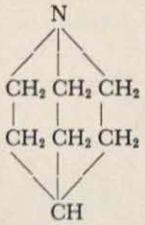
ETHYLAMINE—Ethylamine is a primary amine and has the chemical formula $CH_3CH_2NH_2$.

It freezes at $-80°$ C ($-112°$ F) and boils at 17° C (62.6° F). At ordinary temperatures the compound is a colorless gas with a pungent smell. It has basic characteristics and is highly soluble in water. The white spheres in the model represent hydrogen, the black ones carbon, and the orange one nitrogen.

The nitrogen atom in an amine can also form part of a cyclic molecule. This is the case with piperidine and quinuclidine:



piperidine



quinuclidine

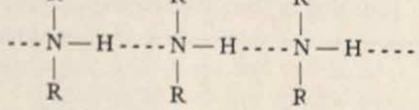
Amines of this type, compared to the simpler amines, require special methods of synthesis. Compounds with several amine groups in the molecule are called diamines, triamines, and so on.

The properties of an amine depend to a considerable extent on the nature of the groups bonded to the nitrogen atom. It is, therefore, conventional to treat aliphatic, alicyclic, aromatic, and heterocyclic amines separately. Mixed amines containing alkyl and aromatic radicals are usually treated as aromatic amines.

Before examining the preparation and reactions of each group, general properties common to all amines will be discussed.

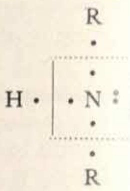
GENERAL PROPERTIES

Hydrogen bonding is a property of all amines. With respect to the secondary amine R_2NH, hydrogen bonding is schematically represented as follows:

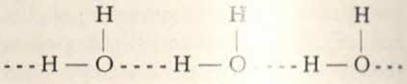


$$\cdots \overset{\displaystyle R}{\overset{|}{\underset{\displaystyle R}{\underset{|}{N}}}} - H \cdots\cdots \overset{\displaystyle R}{\overset{|}{\underset{\displaystyle R}{\underset{|}{N}}}} - H \cdots\cdots \overset{\displaystyle R}{\overset{|}{\underset{\displaystyle R}{\underset{|}{N}}}} - H \cdots\cdots$$

This phenomenon occurs because the amine molecule is polar, and the positively charged hydrogen atom is attracted to the negatively charged portion of an adjacent molecule. This attractive force is to the nitrogen atom of the molecule, in which only three of the five valence electrons are used. The molecule therefore has a free pair of electrons:



Hydrogen bonding occurs also in water and in the alcohols, where the oxygen atom provides the free electron pair:



$$\cdots H - \overset{\displaystyle H}{\overset{|}{O}} \cdots\cdots H - \overset{\displaystyle H}{\overset{|}{O}} \cdots\cdots H - \overset{\displaystyle H}{\overset{|}{O}} \cdots$$

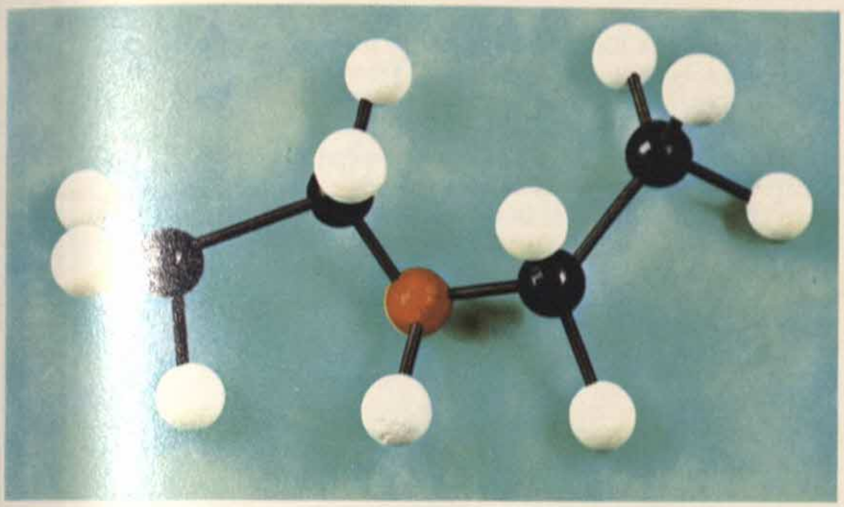
Hydrogen bonds are weak compared to normal chemical bonds. Nevertheless, they have a profound effect on chemical and physical properties. To see how volatility in amines is affected by hydrogen bonds, the following hydrocarbon-amine pairs are compared:

Amine and Analogous Hydrocarbon	Boiling Point °C
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}NH_2$ n-pentylamine	130°
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ n-hexane	69°
$CH_3{-}CH_2{-}NH{-}CH_2{-}CH_3$ diethylamine	55.5°
$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_3$ n-pentane	36°

The close similarities in molecular weight, form, and chain dimensions in the two hydrocarbon-amine pairs should lead to similar boiling points. What actually occurs, however, is a decrease in the volatility of the amines, which involves an increase in boiling point.

The physical properties of tertiary amines are quite different from the physical properties of primary and secondary amines. In fact, there are no hydrogen bonds in tertiary amines, R_3N. Comparison between a tertiary amine and its corresponding hydrocarbon immediately confirms that boiling point is not affected by intramolecular forces:

Amine and Analogous Hydrocarbon	Boiling Point °C
$\begin{array}{c}CH_2{-}CH_3\\ \vert \\ CH_3{-}CH_2{-}N{-}CH_2{-}CH_3\end{array}$ triethylamine	89.5°
$\begin{array}{c}CH_2{-}CH_3\\ \vert \\ CH_3{-}CH_2{-}CH{-}CH_2{-}CH_3\end{array}$ 3-ethylpentane	93.3°

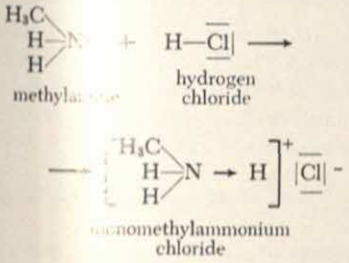


DIETHYLAMINE.—Diethylamine is a secondary amine and has the formula $(CH_3CH_2)_2NH$.

At ordinary temperatures this substance is a liquid like the other secondary and tertiary aliphatic amines of low molecular weight (the exceptions are dimethylamine and trimethylamine, both of which are gases).

Diethylamine freezes at −39° C (−38.2° F) and boils at 55° C (131° F). It is also highly soluble in water.

Amines are bases. They react with acids to yield salts that are generally stable and soluble in water and alcohol. From an electronic point of view, the formation of these salts (alkylammonium salts) occurs as follows (the free electron pairs are shown as line segments):



As can be seen, the nitrogen of the amine uses its free electron pair to bind the proton H^+ of the acid. A bond of this type is called a coordinate covalent bond. It is shown as an arrow pointing in the direction from which the electron pair comes. In normal covalent bonds the electron pair is formed by one electron from each of the two bonding atoms.

The basic character of amines is influenced by the nature of the radicals bonded to the nitrogen atom. Aliphatic amines are stronger bases than ammonia, whereas aromatic amines are weaker bases than ammonia. Aqueous solutions of aliphatic amines give alkaline reactions; the presence of hydroxide ion is explained by the following equilibrium:

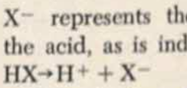
$$\underset{\text{methylamine}}{CH_3NH_2} + H_2O \rightleftarrows [CH_3NH_3]^+ + OH^-.$$

Treating alkylammonium salts with strong bases (NaOH, for example) produces the original amine:

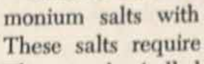
$$\underset{\text{dimethylammonium chloride}}{[(CH_3)_2NH_2]^+Cl^-} + NaOH \rightarrow \underset{\text{dimethyl-amine}}{(CH_3)_2NH} + \underset{\text{sodium chloride}}{NaCl} + H_2O.$$

The nitrogen atom in alkylammonium salts is covalently bonded to one, two, or three radicals, depending on whether the original amine was a primary, secondary, or tertiary amine.

$[R—NH_3]^+X^-$ monoalkylammonium salt



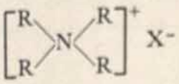
dialkylammonium salt



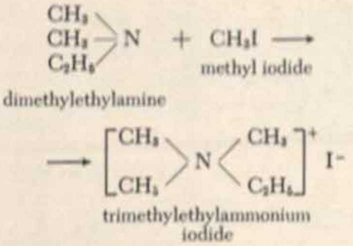
trialkylammonium salt

X^- represents the anion provided by the acid, as is indicated in the reaction $HX \rightarrow H^+ + X^-$

There is also a fourth category of ammonium salts with unusual properties. These salts require separate treatment. They are the 4-alkylammonium salts having the following general chemical formula:



These salts are produced by reactions between tertiary amines and alkyl halides, as follows:



It is interesting to follow formation of this type of salt using a three-dimensional diagram (Illustration 3). The tertiary amine molecule is comparable to a pyramid on a triangular base, with the nitrogen atom at the summit. Following the addition of the alkyl halide, a tetrahedral molecule analogous to organic carbon molecules is formed. When 4-alkylammonium salts are treated with silver hydroxide, 4-alkylammonium hydroxides are produced. These compounds are strong bases; they are comparable to alkaline hydroxides:

$$[(CH_3)_2(C_2H_5)_2N]^+Cl^- + AgOH \rightarrow [(CH_3)_2(C_2H_5)_2N]^+OH^- + AgCl.$$

The fact that 4-alkylammonium salts, unlike mono-, di-, and trialkylammonium salts, will not decompose into amines when treated with caustic soda is due to their stability.

ALIPHATIC AMINES

The first two primary amines, methylamine and ethylamine, are gases with a pungent odor. The next nine (that is, up to eleven carbon atoms) are liquids; all subsequent primary amines are solids. The liquid amines with the lowest boiling points have an unpleasant fishy odor. Secondary and tertiary amines with low molecular weights are liquids, with the exception of dimethylamine and trimethylamine, both of which are gases at ordinary temperatures.

Primary amines are generally soluble in water, ether, and alcohol. Solubility in water, however, diminishes as molecular weight increases.

The three methods described here are often used for the industrial production of alkylamines.

From alcohols and ammonia.—In this reaction, the reagents are exposed to a dehydrating agent. Alumina is often used. The reaction temperature ranges between 300 and 500° C (572 and 932° F):

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} + \underset{\text{ammonia}}{NH_3} \rightarrow \underset{\text{ethylamine}}{C_2H_5NH_2} + H_2O.$$

Amines formed in this manner will subsequently undergo alkylations; mixtures of primary, secondary, and tertiary amines are therefore produced:

$$C_2H_5NH_2 + C_2H_5OH \rightarrow (C_2H_5)_2NH + H_2O.$$

$$(C_2H_5)_2NH + C_2H_5OH \rightarrow (C_2H_5)_3N + H_2O.$$

From nitriles, R−C ≡ N.—Amines are prepared from nitriles by reduction with hydrogen in the presence of suitable catalysts (metallic nickel, for example); these reactions take place at high temperatures and pressures. The reaction is often made to occur in the liquid phase, methyl alcohol being employed as the solvent.

Addition of hydrogen to the triple bond occurs in stages according to the following scheme:

$$\underset{\text{nitrile}}{R{-}C{\equiv}N} \xrightarrow{H_2} \underset{\text{aldimine}}{R{-}CH{=}NH} \xrightarrow{H_2} \underset{\text{primary amine}}{RCH_2{-}NH_2}.$$

These reactions are accompanied by the formation of secondary and tertiary amines:

$$\underset{\text{aldimine}}{R{-}CH{=}NH} + \underset{\text{primary amine}}{RCH_2{-}NH_2} \xrightarrow{-NH_3} R{-}CH{=}N{-}CH_2R$$

$$R{-}CH{=}N{-}CH_2R \rightarrow \underset{\text{secondary amine}}{RCH_2{-}NH{-}CH_2R}$$

These side reactions, however, can be suppressed by carrying out the reduction in the presence of ammonia.

From ammonium and alkyl halides.—This reaction is carried out in a hot alcohol solution, and primary, secondary, and tertiary amines, as well as 4-alkylammonium salts are formed. The reactions are as follows:

$$NH_3 + \underset{\substack{\text{methyl}\\ \text{chloride}}}{CH_3{-}Cl} \rightarrow \underset{\substack{\text{methyl-}\\ \text{ammonium}\\ \text{chloride}}}{(CH_3NH_3)^+Cl^-} \xrightleftharpoons{+NH_3} \underset{\substack{\text{methyl-}\\ \text{amine}}}{CH_3NH_2} + \underset{\substack{\text{ammonium}\\ \text{chloride}}}{NH_4Cl}$$

$$\underset{\text{methylamine}}{CH_3{-}NH_2} + CH_3{-}Cl \rightarrow \underset{\substack{\text{dimethyl-}\\ \text{ammonium}\\ \text{chloride}}}{[(CH_3)_2NH_2]^+Cl^-} \xrightleftharpoons{+NH_3} \underset{\substack{\text{dimethyl-}\\ \text{amine}}}{(CH_3)_2NH} + NH_4Cl$$

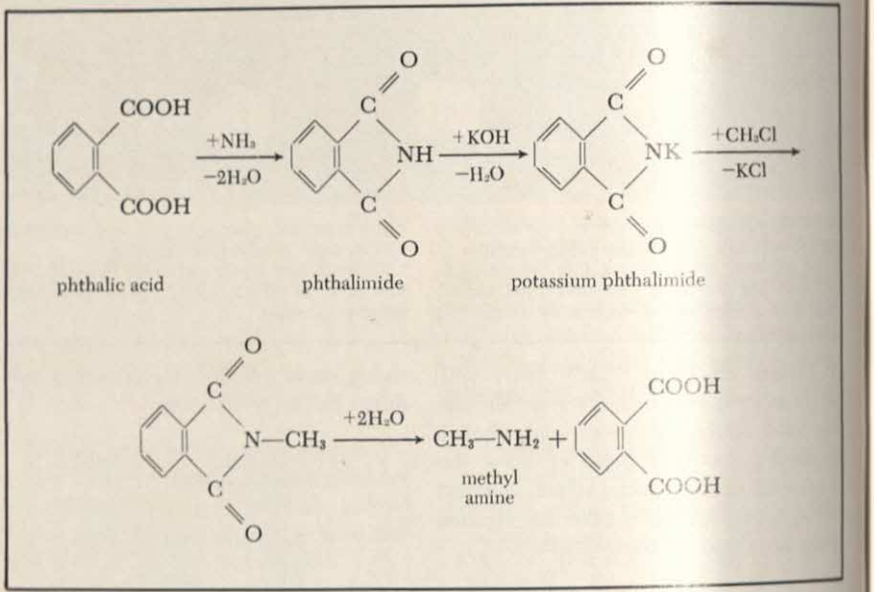
$$\underset{\text{dimethylamine}}{(CH_3)_2NH + CH_3{-}Cl} \rightarrow \underset{\substack{\text{trimethylammonium}\\ \text{chloride}}}{[(CH_3)_3NH]^+Cl^-} \xrightleftharpoons{NH_3} \underset{\text{trimethylamine}}{(CH_3)_3N + NH_4Cl}$$

$$\underset{\text{trimethylamine}}{(CH_3)_3N + CH_3{-}Cl} \rightarrow \underset{\substack{\text{tetramethyl-}\\ \text{ammonium}\\ \text{chloride}}}{[(CH_3)_4N]^+Cl^-}$$

The quantities of the various amines produced can be controlled by varying the reaction conditions. An excess of ammonia, for example, favors formation of the primary amine. A typical industrial preparation is the production of amylamine (five carbon atoms) in an alcohol solution at 165° C (329° F). The reaction yields a mixture of primary amine (about 70 percent) and secondary amine (about 30 percent).

In the laboratory amines are prepared by the last of these three methods, and also by other methods that will now be described.

The Gabriel synthesis.—This method yields pure primary amines and uses the potassium salt of phthalimide:

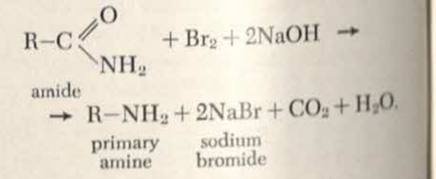


The final reaction is a saponification; it is carried out under alkaline conditions.

Reduction of nitrogen compounds.—This reaction is of considerable importance for the preparation of aromatic amines, although it is rarely used for aliphatic amines.

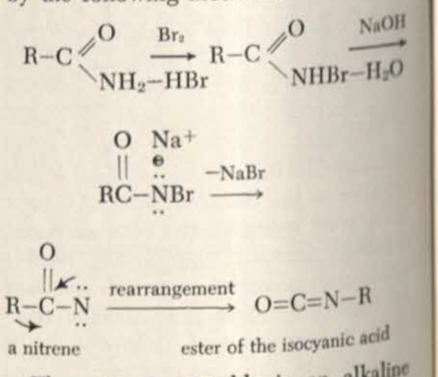
$$\underset{\text{nitroethane}}{C_2H_5 - NO_2} + 3H_2 \rightarrow \underset{\text{ethylamine}}{C_2H_5 - NH_2} + 2H_2O.$$

The Hofmann reaction.—The amides of carboxylic acids, when treated with bromine and alkali, can be converted into primary amines with a decrease of one carbon atom in the molecule:



$$\underset{\text{amide}}{R{-}C(=O){-}NH_2} + Br_2 + 2NaOH \rightarrow \underset{\substack{\text{primary}\\ \text{amine}}}{R{-}NH_2} + \underset{\substack{\text{sodium}\\ \text{bromide}}}{2NaBr} + CO_2 + H_2O.$$

The formation of the amine is explained by the following mechanism:



$$R{-}C(=O){-}NH_2 \xrightarrow[-HBr]{Br_2} R{-}C(=O){-}NHBr \xrightarrow[-H_2O]{NaOH} RC(=O){-}\ddot{\underset{..}{N}}{}^{\ominus}Br\ Na^+ \xrightarrow{-NaBr} \underset{\text{a nitrene}}{R{-}C(=O){-}\ddot{\underset{..}{N}}} \xrightarrow{\text{rearrangement}} \underset{\text{ester of the isocyanic acid}}{O{=}C{=}N{-}R}$$

The ester is unstable in an alkaline medium and is transformed into the

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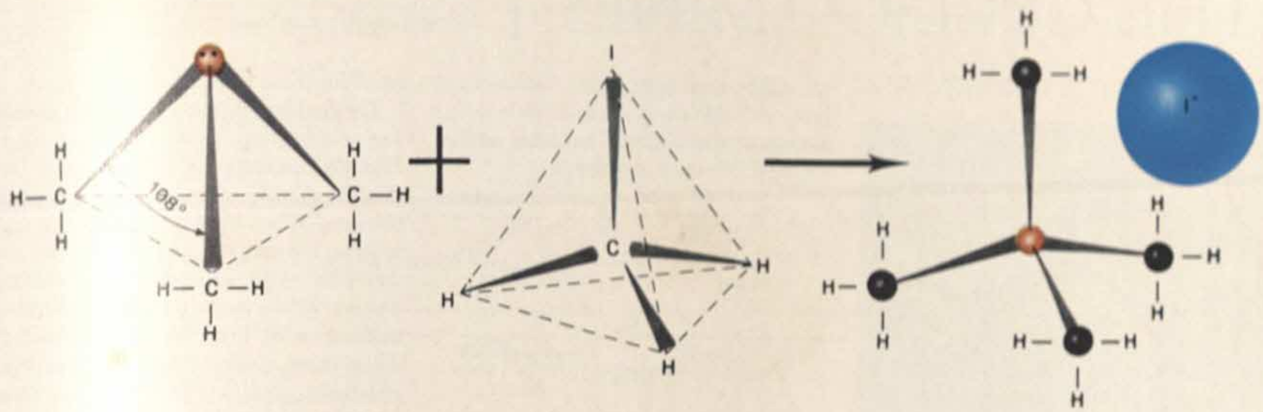

THE FORMATION OF TRIMETHYLAMINE—Trimethylamine which has the chemical formula $(CH_3)_3N$, is a tertiary amine with a pair of free electrons on the nitrogen atom. This diagram shows the structure of the molecule as a pyramid with a triangular base. The nitrogen atom is located at the summit. Addition of methyl iodide (a tetrahedral molecule with the chemical formula CH_3I) produces tetramethylammonium iodide, $[(CH_3)_4N]^+I^-$. In this compound the tetramethylammonium ion consists of four $-CH_3$ groups arranged in a tetrahedral pattern arround the nitrogen atom. This arrangement is analogous to the structure of organic carbon compounds.

amine:

$$R{-}N{=}C{=}O \xrightarrow{H_2O} RNH_2 + CO_2.$$

The Schmidt reaction.—Primary amines can be obtained from carboxylic acids by treatment with hydrazoic acid in the presence of sulfuric acid:

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{hydrazoic acid}}{HN_3} \rightarrow \underset{\text{methylamine}}{CH_3NH_2} + CO_2 + N_2.$$

The formation of amines and diamines from amino acids during natural fermentation processes will be discussed in the article on amino acids.

CHARACTERISTIC REACTIONS

As described, methods for the preparation of amines often lead to mixtures of primary, secondary, and tertiary amines.

A reaction frequently used for separations employs benzene sulfonyl chloride. For example, tertiary amines will not react at all in a basic solution, whereas primary and secondary amines form the corresponding benzene sulfonamides:

$$CH_3{-}NH_2 + \underset{\text{benzene sulfonyl chloride}}{C_6H_5{-}SO_2{-}Cl} \rightarrow CH_3{-}NH{-}SO_2{-}C_6H_5 + HCl.$$

$$(CH_3)_2NH + C_6H_5{-}SO_2{-}Cl \rightarrow (CH_3)_2N{-}SO_2{-}C_6H_5 + HCl.$$

The three amines are then separated by making use of the following factors:

a. The unchanged tertiary amine can be distilled from the mixture.

b. The benzene sulfonamide derived from the primary amine forms a sodium salt and remains in solution.

c. The benzene sulfonamide of the secondary amine does not form a salt and remains undissolved.

The free amines can be produced from the benzene sulfonamides by treating with acid. For example, consider the reaction with nitrous acid. Primary amines are generally converted into primary alcohols as the result of the loss of nitrogen:

$$R{-}CH_2{-}NH_2 + \underset{\text{nitrous acid}}{HO{-}N{=}O} \rightarrow R{-}CH_2{-}OH + N_2 + H_2O.$$

Secondary amines are converted into nitrosamines:

$$R_2NH + HO{-}N{=}O \rightarrow \underset{\text{a nitrosamine}}{R_2N{-}NO} + H_2O.$$

Tertiary amines, once again, will not be attacked.

An important characteristic reaction of primary amines occurs with chloroform and alkalis:

$$R{-}NH_2 + \underset{\text{chloroform}}{CHCl_3} + 3KOH \rightarrow \underset{\text{an isonitrile}}{R{-}NC} + 3KCl + 3H_2O.$$

The strong and characteristic odor of the isonitriles is a test for the presence of a primary amine.

METHYLAMINES

Methylamines are produced on an industrial scale by the method described above. The mono-, di-, and trimethylamines are then separated by distillation. Trimethylamine is also produced by heating molasses residues. The methylamines are used principally as raw materials for the preparation of numerous other products. Some of these are shown in the following equations:

from CH_3NH_2 and $ClCH_2{-}COONa$ → n-lauroilsarcosine (additive for toothpaste)

from CH_3NH_2 and hydroquinone → p-methylaminophenol (photographic developer)

from $(CH_3)_2NH$ and carbon disulfide → zinc dimethylcarbamate (fungicide)

from $(CH_3)_2NH$ and methyl formate → dimethylformamide (solvent)

ETHYLAMINES

Monoethylamine is used as a selective solvent and as an intermediate for the preparation of special additives for the textile industry.

Diethylamine is used in the preparation of a series of insecticide products, pharmaceuticals, accelerators for the processing of rubber, and corrosion inhibitors.

Triethylamine is used as a corrosion inhibitor, particularly in industrial plants where the circulating chemicals include chlorinated solvents.

BUTYLAMINES

Butylamines are produced industrially by means of a special method in which ammonia, n-butyl alcohol, and hydrogen are passed over a nickel-base catalyst at a temperature of 190° C (374° F). This produces a mixture of the three amines. The fatty acid salts of these three amines have pronounced emulsifying properties. They are, therefore, used as flotation agents and as special purpose soaps. Amines have antioxidizing properties; they are thus used as additives to gasoline and diesel fuels to prevent polymerization of unsaturated fuel components by the oxygen of air.

THE CYCLIC AMINES | aromatic, alicyclic, and heterocyclic amines

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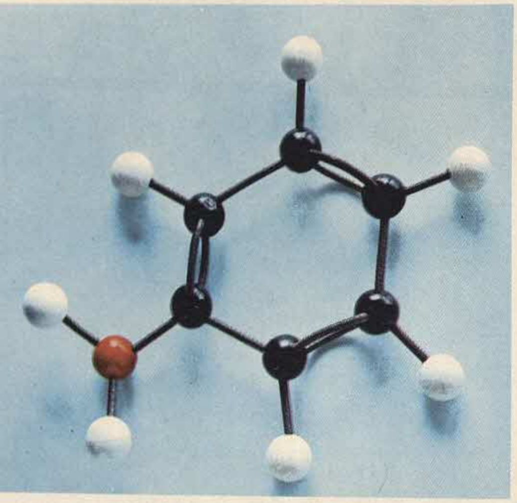
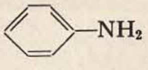


ANILINE—Aniline is found in small quantities in coal tar. It is an oily and colorless liquid when pure, although it quickly turns brown when exposed to air and light. It has a characteristic odor and is poisonous. When cooled to about −10° C (14° F), it freezes into a white crystalline mass. It boils at 184° C (363.2° F). Aniline is the raw material for the preparation of many dyes. It is often used also as a reagent in the laboratory.

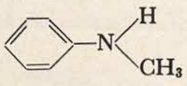
The general properties of amines and alkyl amines were discussed in a previous article. This article treats aromatic, alicyclic, and heterocyclic amines.

AROMATIC AMINES

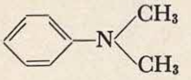
The simpler members of this group, such as aniline and mono- and dimethyl aniline, are colorless and oily liquids with a slightly aromatic odor. The higher amines, on the other hand, are solids.



aniline

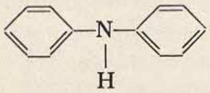


methyl aniline

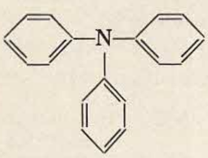


dimethyl aniline

As mentioned previously, aromatic amines are less basic than aliphatic amines. Moreover, there is a gradual reduction in basic character as the number of aromatic radicals bonded to the nitrogen atom increases (diphenylamine forms salts only with strong acids).



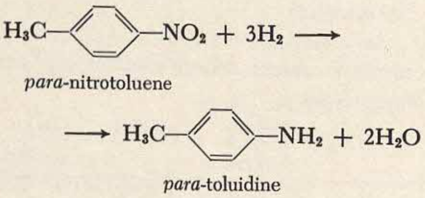
diphenylamine



triphenylamine

PREPARATION

a. The most common method for the preparation of aromatic amines is reduction of the corresponding nitro derivatives:



This method is suitable for both laboratory and industrial scale production. The nitro derivatives used as starting materials are obtained by nitration of aromatic hydrocarbons; mixtures of nitric acid and concentrated sulfuric acid are used for these nitrations.

The simpler (primary) aromatic amines are colorless liquids or crystalline solids that are sparingly soluble in water but readily soluble in the common organic solvents. When heated with alkyl or aryl iodides, the primary aromatic amines are converted into secondary and tertiary amines. When heated with concentrated sulfuric acid, they become sulfonated. They form condensation products with aldehydes, and they form anilides when heated with organic acids. When warmed with a solution of nitrous acid, they are converted into phenols. They give the isonitrile reaction when warmed with chloroform and a caustic alkali.

Reduction of the nitro group generally takes place with a gradual substitution of hydrogen for the oxygen. Thus, depending upon the reducing agent and reaction conditions, either the required amine or an intermediate compound can be produced.

The most frequently used reducing agents are:

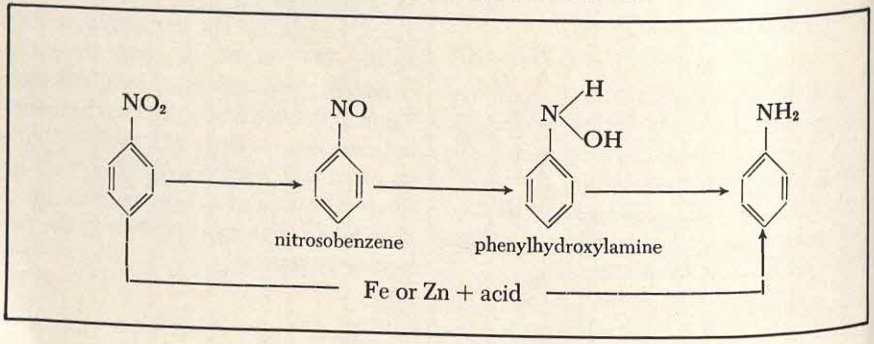
1. Hydrogen activated with suitable catalysts, metallic nickel or cobalt, for example.
2. Nascent hydrogen obtained from metals (zinc, iron) and acids or caustic soda according to the reactions

$$Zn + 2HCl \rightarrow ZnCl_2 + H_2.$$
$$Zn + 2NaOH \rightarrow Na_2ZnO_2 + H_2.$$

3. Alcohols, which carry out the reduction in alkaline solution and are oxidized to aldehydes.
4. Compounds of bivalent tin, which are converted into derivatives of tetravalent tin as a result of the reduction.
5. Ammonium sulfide and alkaline sulfides.

As the schematic diagrams of the various reactions show, the reaction environment (acid or alkaline) has a decisive effect on the reduction process and on the nature of the intermediate compounds:

Acid environment:



METHYLANILINE—This is a mixed secondary amine whose chemical formula is $C_6H_5NHCH_3$. Methylaniline is a liquid at ordinary temperatures. It solidifies at −57° C (−70.6° F) and boils at 196° C (384.8° F), and is only slightly soluble in water. Methylaniline is prepared industrially by heating aniline ($C_6H_5NH_2$) with methyl alcohol (CH_3OH) and hydrochloric acid (HCl) to 180° C (356° F) in an autoclave.

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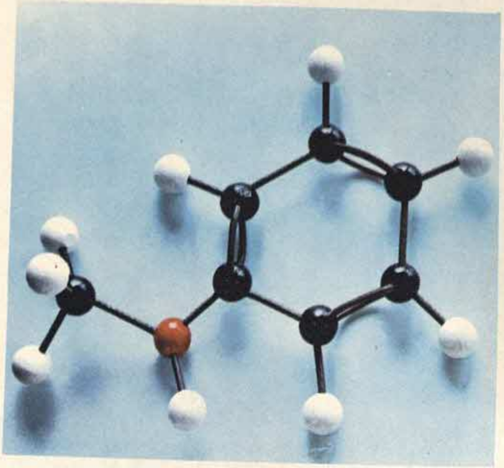
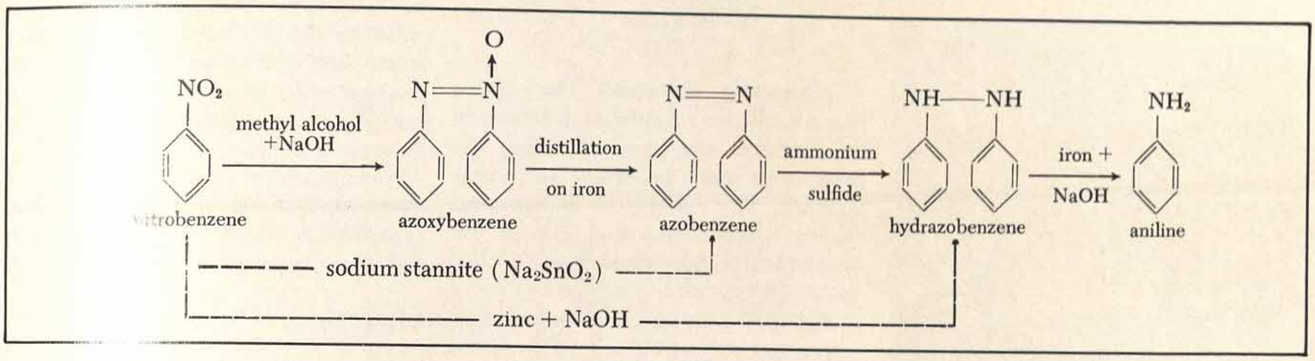
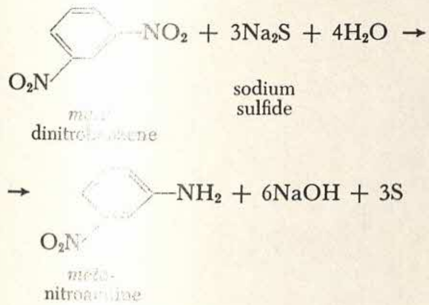


Alkaline environment:



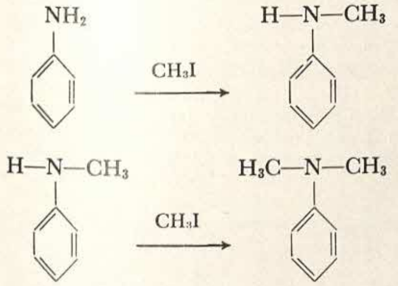
As these reactions indicate, reduction with iron or zinc in an acid environment is preferred to produce the amine directly. Catalytic hydrogenation is widely used in industrial processes. This will be discussed in greater detail when aniline is discussed.

Alkaline sulfides are particularly suitable for the partial reduction of polynitro derivatives:



$-NO_2 + 3Na_2S + 4H_2O \rightarrow$
O_2N
sodium sulfide
meta-dinitrobenzene
$\rightarrow -NH_2 + 6NaOH + 3S$
O_2N
meta-nitroaniline

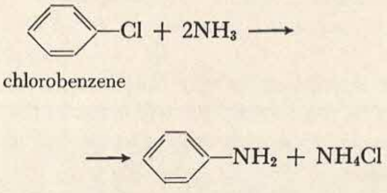
b. Direct alkylation of aniline with alkyl halides is suitable for the preparation of mono- and dialkylanilines:



Analogously to what happens in the case of the aliphatic amines, quaternary ammonium salts are also produced.

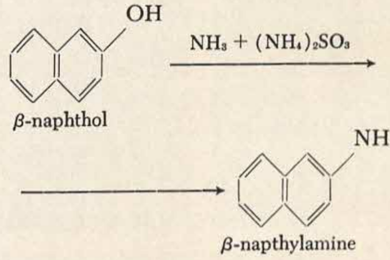
Alkylation with alcohols is used in industrial processes. Dimethylaniline is prepared by heating aniline with methyl alcohol in an autoclave in the presence of small quantities of sulfuric acid.

c. Another method of preparation—one that presents some practical difficulties—consists in substituting an aromatic group for a hydrogen atom of the ammonia. This method calls for temperatures in excess of 200° C (392° F) and very high pressures with a catalyst of metallic copper or copper(I) chloride:



$-Cl + 2NH_3 \longrightarrow$
chlorobenzene
$\longrightarrow -NH_2 + NH_4Cl$

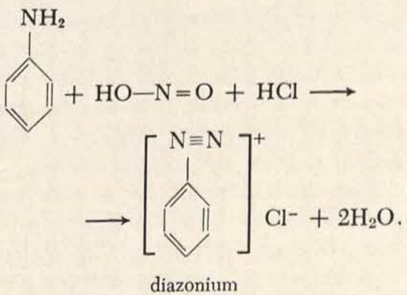
d. The Bucherer reaction is suitable exclusively for the preparation of aromatic amines—particularly naphthylamine. This reaction consists of heating phenols with ammonia and ammonium sulfite in an aqueous solution:



CHARACTERISTIC REACTIONS

Some reactions are common to both aliphatic and aromatic amines. These include alkylation with acid chlorides and the formation of isonitriles, which have already been described. The following reactions require special treatment.

Reactions with nitrous acid.—Primary amines are converted into diazonium salts by reaction with nitrous acid and hydrochloric acid at temperatures below 10° C (50° F):

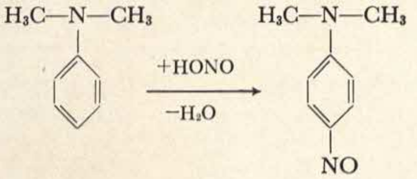


diazonium chloride

As indicated in the formula, diazonium salts are extensively dissociated in aqueous solutions.

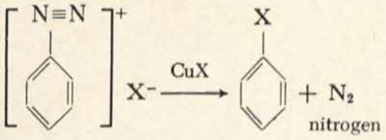
Secondary amines, on the other hand, are converted into nitrosamines in a manner analogous to the corresponding aliphatic amines.

Tertiary amines undergo substitutions in the aromatic nucleus:



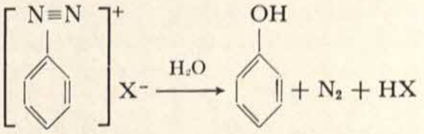
Diazonium salts merit special comment because of their reactivity and their usefulness in the synthesis of various aromatic derivatives. The following reactions are examples:

If copper(I) chloride or bromide is added to the solution of the salt, an aromatic chloride or bromide (Sandmayer's reaction) is produced:



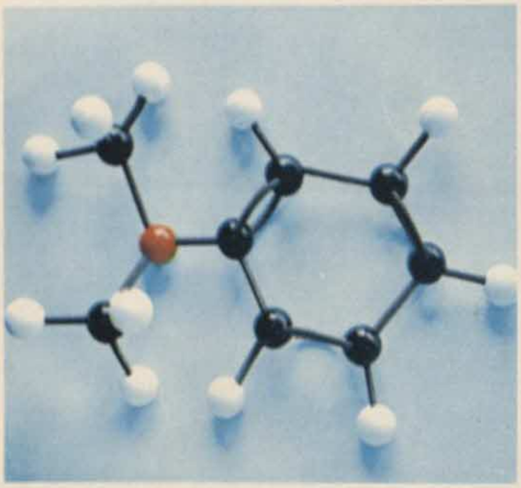
The same synthesis can be obtained by means of Gattermann's reaction. In this case copper in powder form and a halogen acid are used. Slightly different methods produce all the other aryl halides from diazonium salts.

Diazonium salts react with water to yield phenols:



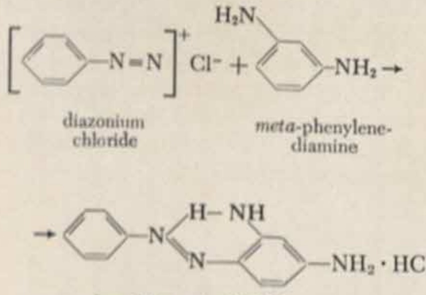
The importance of aromatic amines from the preparation point of view is often associated with the formation of diazonium salts as intermediate compounds. Even the azo dyes are produced from aromatic

3



DIMETHYLANILINE — This compound freezes at 3° C (37.4° F) and boils at 194° C (381.2° F). It is prepared by heating a mixture of aniline, methyl alcohol, and concentrated sulfuric acid to 730 to 735° C (1,346 to 1,355° F) at a pressure of 25 to 30 atmospheres. The reaction gives a 90 percent yield.

amines via diazonium salts. These are generally made to react with aromatic compounds amenable to substitution in the *ortho-* or *para-* positions of the nucleus. Such compounds are phenols, naphthols, amines, and naphthylamines:



chrysoidine y (reddish brown color)

(The dye, which is basic, is in this case converted into a salt with HCl. As shown, a hydrogen bond is present inside the molecule).

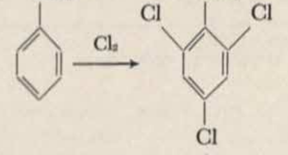
Azo dyes, characterized by the presence of one or more $-N{=}N-$ groups, have varied applications and are produced on a vast scale. More than half of the 2,250 dyes of commercial interest belong to this class. Typical applications are the dyeing of wool, silk, cotton, paper, and synthetic fibers, as well as the coloring of varnishes, paints, inks, cosmetics, plastic materials, and foodstuffs.

Oxidation reactions.—Primary and secondary aromatic amines are more sensitive to oxidation than aliphatic amines. The color they take on when exposed to air is explained by the formation of oxidation products.

Tertiary amines are converted into amine oxides by special oxidizing agents:

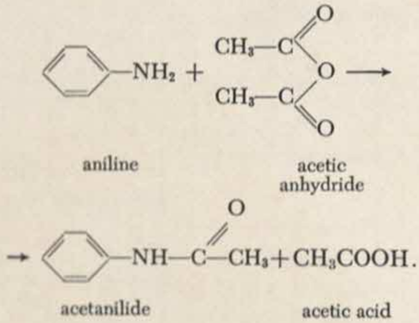
$$R_3N \xrightarrow{\text{oxidizing agent}} R_3N \rightarrow O.$$

Substitution reactions. — The amine group facilitates substitution reactions in the aromatic nucleus by directing the substituents into the *ortho-* and *para-*positions. The reaction of aniline with chlorine leads to the formation of the symmetrical trichloroderivative:



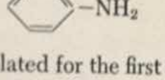
It is interesting to note that in an acid solution the substitution will occur in the *meta-* position with respect to the amine group.

In many substitution reactions in the aromatic nucleus it is desirable to protect the amine group. This is to prevent attack by the reagents being employed. The following conversion into the acetyl derivative accomplishes this purpose very well:



The amine group can then be regenerated from the acetyl derivative by hydrolysis in the presence of mineral acids.

ANILINE



Aniline, isolated for the first time in 1826, is a colorless liquid (boiling point: 184° C or 363.2° F) that turns brown when it is exposed to air. It is produced industrially by the following methods.

Catalytic reduction of nitrobenzene. A mixture of hydrogen and nitrobenzene in the vapor state is heated to 350° C (662° F) and passed over catalysts that vary from process to process and may consist of copper salts, nickel or molybdenum sulfides, and metallic oxides.

Reduction of nitrobenzene with iron and hydrochloric acid in an aqueous solution (Béchamp process). This method was used for a long time, but has now been completely replaced by catalytic reduction for large-scale production because catalytic reduction has economic advantages and produces a purer product.

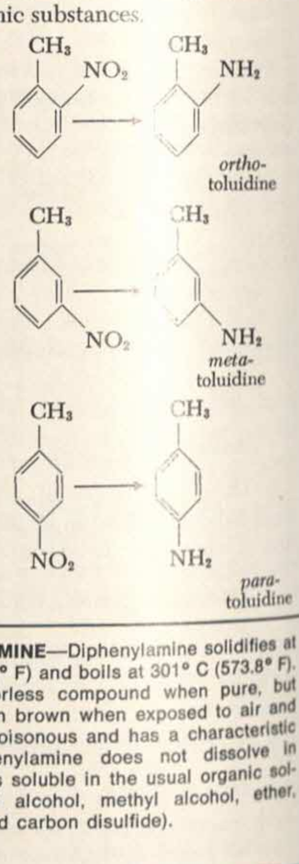
Aniline can also be produced by the reaction between chlorobenzene and ammonia in water at a high temperature and under pressure, with copper(I) chloride acting as catalyst.

Aniline is used for the preparation of dyes, additives for the rubber industry (accelerators and antioxidizing agents), and pharmaceutical products.

TOLUIDINE

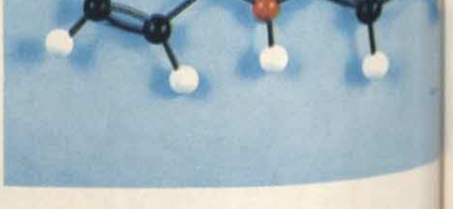
The three toluidines, *ortho-*, *meta-*, and *para-*, are prepared by catalytic reduction of the corresponding nitrotoluenes.

Toluidines are used for producing synthetic dyes and for the preparation of other organic substances.



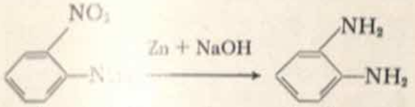
DIPHENYLAMINE—Diphenylamine solidifies at 54° C (129.2° F) and boils at 301° C (573.8° F). It is a colorless compound when pure, but tends to turn brown when exposed to air and light. It is poisonous and has a characteristic odor. Diphenylamine does not dissolve in water, but is soluble in the usual organic solvents (ethyl alcohol, methyl alcohol, ether, benzene, and carbon disulfide).

4

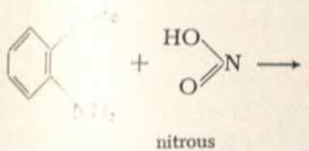


PHENYLENEDIAMINE

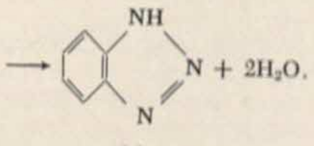
Ortho-phenylenediamine is prepared by reduction of *ortho*-nitroaniline:



These substances have a tendency to form cyclic compounds; the following is an example:



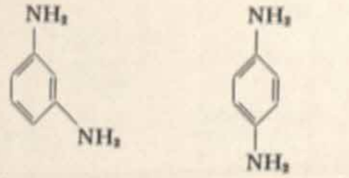
nitrous acid



azimidobenzene

Meta-phenylenediamine, which is produced by reduction of the corresponding dinitrobenzene, can be used to derive an azo dye known as Bismarck brown.

Para-phenylenediamine is formed from *para*-nitroaniline by means of reduction and forms the basis of numerous other dyes.

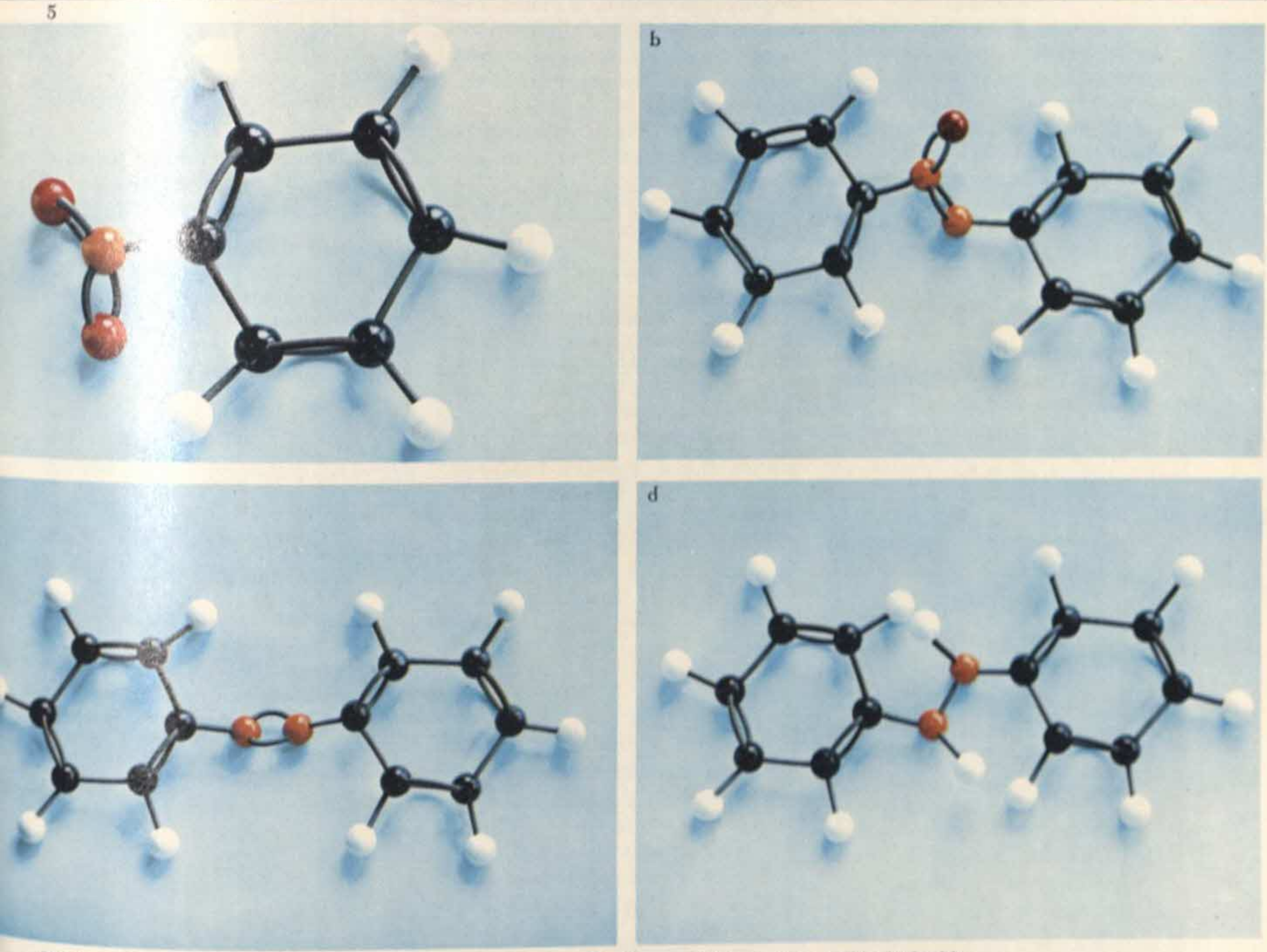


meta-phenylenediamine *para*-phenylenediamine

ADRENALINE

Adrenaline is a hormone secreted by the medulla of the adrenal gland. It regulates cell metabolism in the organism, increases blood pressure, and speeds heart action.

Adrenaline can be classified among the secondary amines; it is produced by the

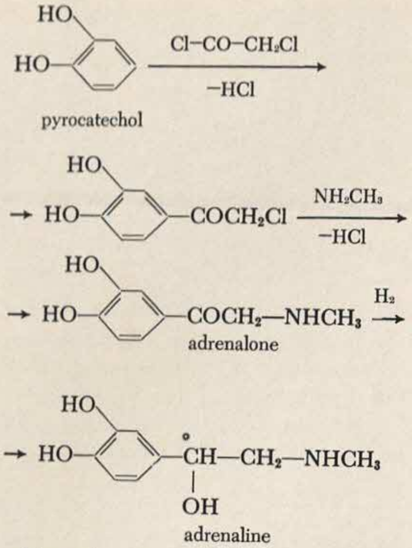


FROM NITROBENZENE TO ANILINE—Aniline is produced by catalytic reduction of nitrobenzene, $C_6H_5NO_2$ (Illustration 5a). When the reduction is carried out in an alkaline medium, a series of substances that correspond to the various stages of the reduction can be prepared. Treating nitrobenzene with sodium hydroxide (NaOH) and methyl alcohol (CH_3OH) produces a yellow solid called azoxybenzene: $H_5C_6-N(O)=N-C_6H_5$ (Illustration 5b). Distilling this compound on iron yields azobenzene, a solid with a reddish brown color: $H_5C_6-N=N-C_6H_5$ (Illustration 5c). Finally, treating the azobenzene with ammonium sulfide produces hydrazobenzene, a white solid (Illustration 5d). Reduction of hydrazobenzene then yields two molecules of aniline (shown in Illustration 1).

Azobenzene can also be produced by reacting nitrobenzene with sodium stannite. Similarly, hydrazobenzene can be obtained directly by reacting nitrobenzene with zinc and sodium hydroxide.

The medium in which the reduction of the nitro group takes place has a decisive effect both on the development of the reaction and on the nature of the intermediate compounds. If the reduction is carried out in an acid medium rather than an alkaline medium, the intermediate compounds will be different from those shown in Illustrations 5b, 5c, and 5d. In this case the intermediates would be nitrosobenzene and phenylhydroxylamine.

following synthesis:

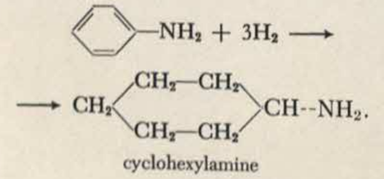


The adrenaline molecule contains an asymmetric carbon atom (shown by the asterisk). Since only one of the optical isomers is physiologically active, the racemic mixture produced by this reaction must be separated if the adrenaline is to be used for pharmaceutical purposes.

ALICYCLIC AMINES

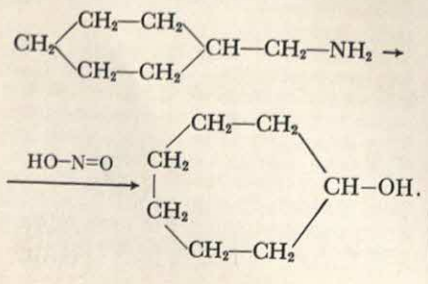
This group of amines, which contains one or more nonaromatic hydrocarbon rings bonded to the nitrogen atom, exhibits properties and reactions similar to those of aliphatic amines.

One method of preparation is reduction of the corresponding aromatic amine with catalytically activated hydrogen:

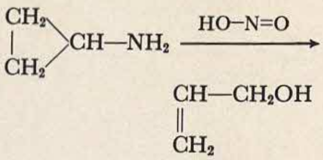


Cyclohexylamine can also be produced by reductive amination of cyclohexanone (an alicyclic ketone) in the presence of nickel.

The reaction of primary amines with nitrous acid merits special comment because the formation of the alcohol in this case is accompanied by enlargement of the hydrocarbon ring:



Cyclopropylamine is an exception to this rule and reacts by opening the ring:

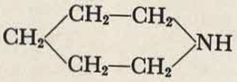


Cyclohexylamine is a liquid that boils at 134° C (273.2° F). It is used for the preparation of insecticides, plasticizers, and corrosion inhibitors.

HETEROCYCLIC AMINES

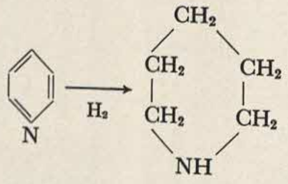
As mentioned previously, compounds containing a nitrogen atom inserted in a saturated or unsaturated ring often have properties characteristic of amines. These compounds are, therefore, referred to as heterocyclic amines. Both the methods of preparation and the properties of these compounds differ widely. It will, therefore, be best to give separate consideration to some of the most important members of this group.

PIPERIDINE



Piperidine is a liquid that is miscible with water. It is characterized by the same properties as aliphatic amines. In particular, it has a basicity close to that of diethylamine.

The most important method of preparation consists of reduction of pyridine:

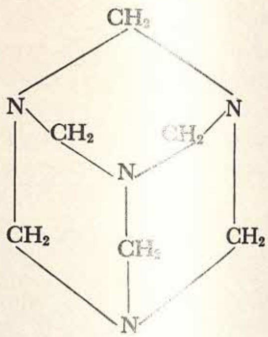


This reduction is accomplished with sodium and alcohol or with catalytically activated hydrogen.

UROTROPIN

Urotropin (hexamethylene tetramine) merits special mention because of its importance in the pharmaceutical field. It is used as a disinfectant of the urinary canals.

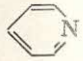
As the structural formula given below indicates, it is probably a cyclic tetramine:



Urotropin is produced on an industrial scale from low-cost raw materials—formaldehyde and ammonia:

$$6\ HCHO + 4\ NH_3 \rightarrow 6\ H_2O + \underset{\text{urotropin}}{C_6H_{12}N_4}.$$

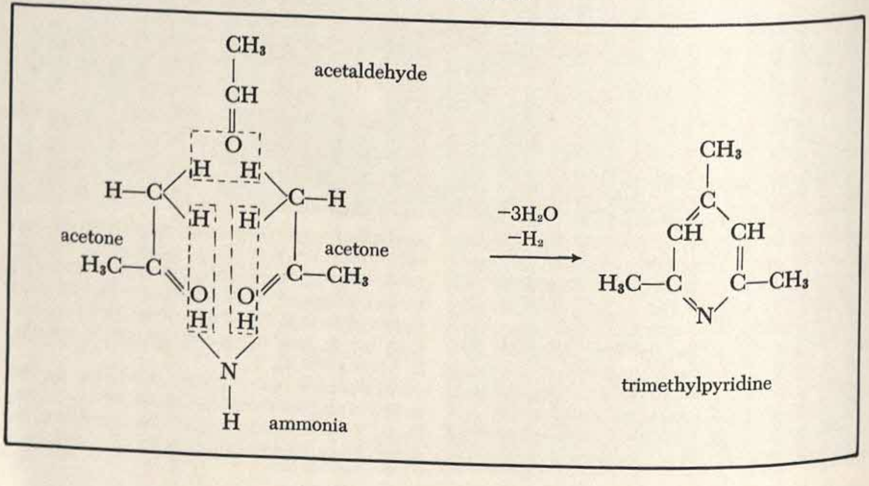
PYRIDINE



Pyridine is a liquid with a penetrating and very unpleasant odor. It is miscible with water and is also a solvent for organic compounds and inorganic salts.

Chemically, pyridine behaves as a weak tertiary base. It forms salts with acids and tetra-alkylammonium compounds with alkyl halides.

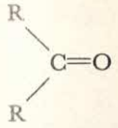
The pyridine molecule has an electron arrangement analogous to benzene. Pyridine and its methyl derivatives—the methyl-pyridines—are used primarily as solvents. They are also used to denature alcohol.



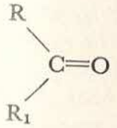
THE KETONES | their industrial importance and theoretical interest

The term *ketone* is derived from the name of the simplest but most important member of this series, acetone. In several reactions, ketones are similar to aldehydes, although less marked in variety. The range of application of ketones is wide; they are used in medicine, insecticides, celluloids, and lacquers. Regulated reduction of ketones produces secondary alcohols; vigorous reduction produces the corresponding hydrocarbons.

If R and R_1 represent two hydrocarbon radicals and $>C=O$ is the carbonyl function, then ketones are represented as follows:



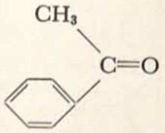
as a simple ketone, and



as a mixed ketone.

R and R_1 can represent aliphatic, alicyclic, aromatic, or heterocyclic groups. If one of the R groups is replaced by hydrogen, an aldehyde is formed. These two classes of organic compounds have analogous properties that can be noted in the methods of their preparation and their characteristic reactions. However, the difference in substitution affects the nature of the carbonyl and causes differences in reactivity.

The different ketones are named by specifying the two radicals bound to the $>C=O$. For example,



as methyl phenyl ketone; or (by referring to the corresponding hydrocarbon and using the suffix *-one*),

$$CH_3-CH_2-CH_2-CH_2-CH_3,$$

as pentane and

$$CH_3-CO-CH_2-CH_2-CH_3,$$

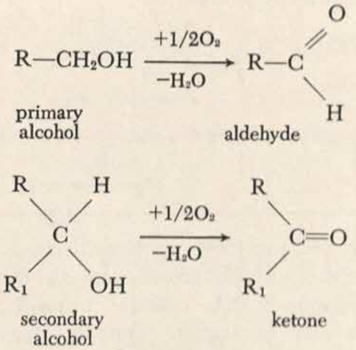
as 2-pentanone (methyl propyl ketone). Ketones corresponding to the lower members of the aliphatic hydrocarbon series are liquids that are miscible with water and characteristically have a pleasant smell. The higher members (those with more than 11 carbon atoms) are solids.

The liquid ketones are solvents for a large variety of organic compounds and are used in the preparation of paints—particularly nitrocellulose paints and those with a base consisting of ethers and esters of cellulose.

PREPARATION

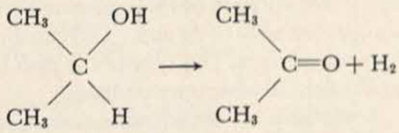
The principal materials from which ketones are made are similar to those used in the preparation of aldehydes, alcohols, carboxylic acids, and unsaturated hydrocarbons.

Aldehydes are prepared from primary alcohols; ketones are prepared from secondary alcohols, as shown below.



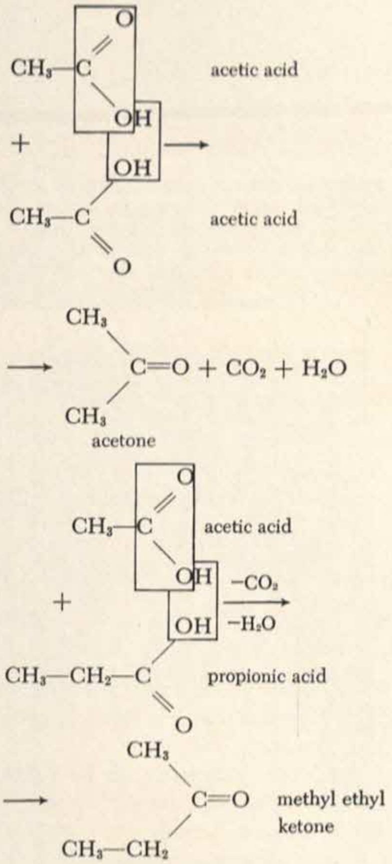
The oxidation reaction used is of considerable industrial importance. The reaction takes place at high temperatures, with copper- or silver-based catalysts. Air is the oxidizing agent.

A related method is dehydrogenation in the absence of oxygen. This reaction is generally carried out at 400 to 600° C (752 to 1,112° F) with metallic oxides as catalysts:



The laboratory preparation uses the oxidation of secondary alcohols. The reaction takes place in the liquid phase, with sodium bichromate ($Na_2Cr_2O_7$) and sulfuric acid (H_2SO_4) used as oxidizing agents. This has a parallel in the preparation of aldehydes.

Ketones can be prepared from carboxylic acids, although this method is of limited industrial importance at the present. The reactions take place in the vapor phase, at 400 to 500° C (752 to 932° F). Oxides of manganese, thorium, or cerium are the catalysts that provide a surface for the reaction to take place, as shown by the following structure:

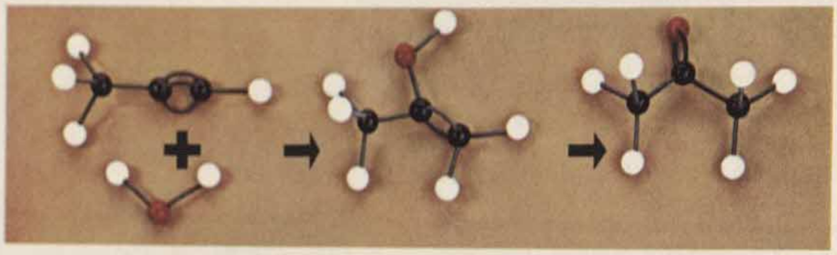


This preparation can thus be used for both simple and mixed ketones: simple

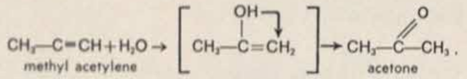
1

CYCLOPENTADECANONE—A saturated cyclic ketone with the chemical formula $(CH_2)_{14}CO$, cyclopentadecanone has a waxy appearance and a musky odor. Its commercial name is Hexaltone. This ketone, mixed with other compounds, is used in the perfume industry.

2

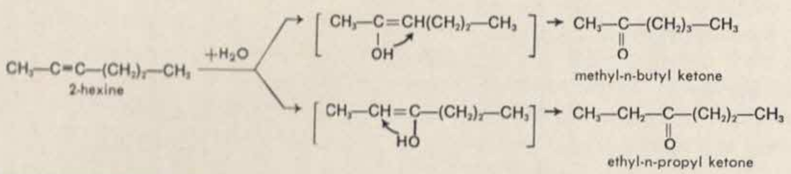


PREPARATION OF KETONES FROM HYDROCARBONS—The hydrocarbons of the acetylene series—except for acetylene itself—can be used to synthesize ketones by hydration in the presence of sulfuric acid and a salt of mercury. This reaction, which is analogous to the hydration of acetylene to acetaldehyde, first forms an unstable hydroxylated intermediate that is immediately converted into a ketone:



$$CH_3{-}C{\equiv}CH + H_2O \rightarrow \left[CH_3{-}\overset{OH}{C}{=}CH_2 \right] \rightarrow CH_3{-}\overset{O}{\overset{\|}{C}}{-}CH_3 .$$

Some reactions lead to the formation of the two ketone isomers, due to the fact that water can be added to the double bond in two different ways. An example is the hydration of 2-hexyne to yield methyl-n-butyl ketone and ethyl-n-propyl ketone.

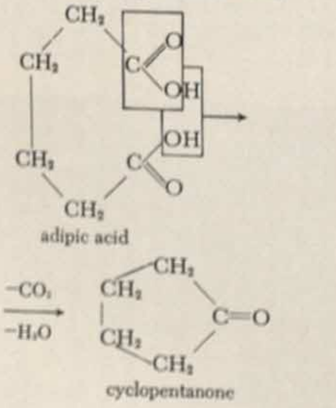


$CH_3{-}C{\equiv}C{-}(CH_2)_2{-}CH_3$
2-hexine
$+H_2O$
$CH_3{-}C{=}CH(CH_2)_2{-}CH_3$
OH
$CH_3{-}C{-}(CH_2)_3{-}CH_3$
O
methyl-n-butyl ketone
$CH_3{-}CH{=}C{-}(CH_2)_2{-}CH_3$
HO
$CH_3{-}CH_2{-}C{-}(CH_2)_2{-}CH_3$
O
ethyl-n-propyl ketone

ketones are made from a single acid; mixed ketones from a mixture of two different acids.

Analogous reactions can be obtained by heating calcium, barium, or zinc salts of the carboxylic acids.

Cyclic ketones are prepared by extending this method to the dicarboxylic acids. An example is cyclopentadecanone:

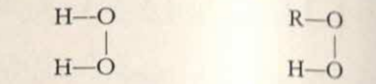


The yield of these reactions depends on the ring size. Cyclopentanone and cyclohexanone—which contain, respectively, five and six carbon atoms—are formed more easily than ketones with seven or eight carbon atoms. Yields are minimal for rings with 9 to 13 carbon atoms, but tend to become greater with larger rings.

Ketones can also be prepared by reacting chlorides of the carboxylic acids or nitriles (corresponding to the carboxylic acids) with Grignard reagents, named for the French chemist Victor Grignard; see structure below.

The first part of the reaction consists of the addition of the organometallic reagent to the $>$C=O and −C≡N in anhydrous solvents. This type of reaction is used solely in laboratory synthesis.

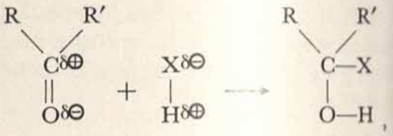
A method of considerable industrial importance for the joint preparation of hydroxylated compounds and ketones is the decomposition of organic hydroperoxides. These latter chemicals are considered as derivatives of hydrogen peroxide:



hydrogen peroxide hydroperoxide

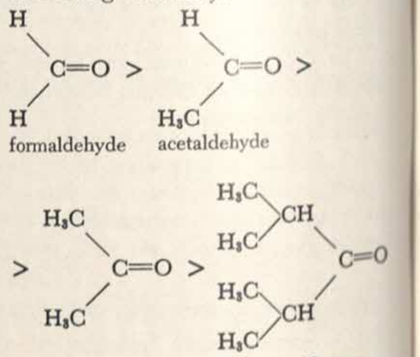
Some hydroperoxides are obtained by direct oxidation of hydrocarbons (such as cumene).

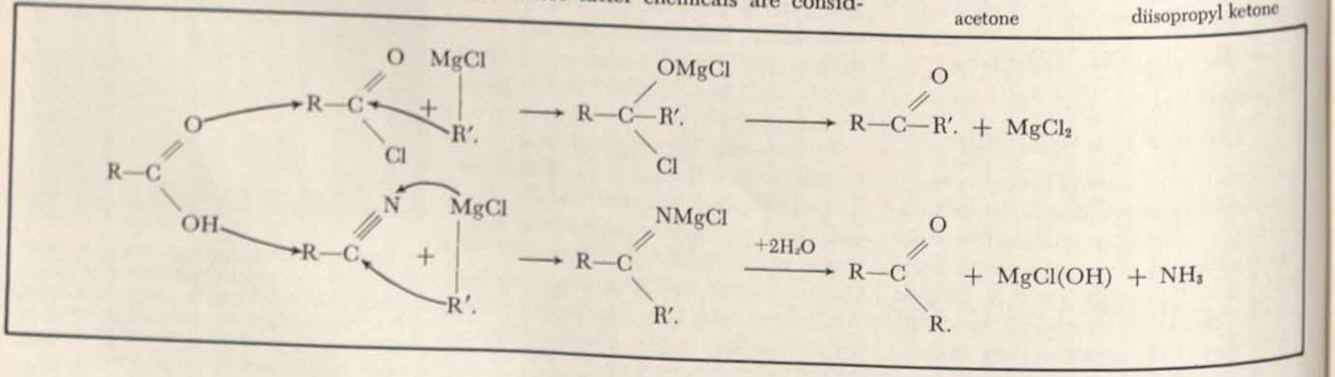
As in the case of aldehydes, many of the reactions that affect the carboxylic group in ketones occur by an addition mechanism represented in its most general form below:



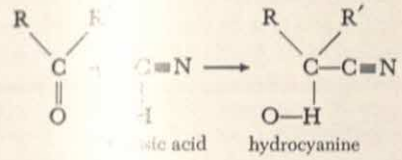
where H−X represents a polar compound (for example, H−CN).

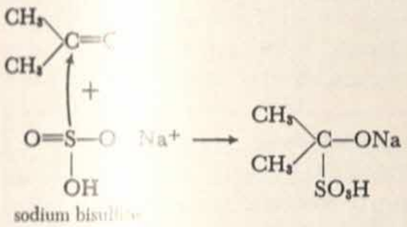
In general, differences in reactivity exist between aldehydes and ketones, due to the different steric impediments of the substituents. The greater the size of the groups bound to the $>$C=O, the more they interfere with the reagent molecule by blocking its access to the double bond. In aldehydes, at least one substituent is hydrogen. Because hydrogen affords the least possible steric hindrance, the reactivity of aldehydes is generally greater than that of ketones. Formaldehyde—with two hydrogen atoms bound to the carbonyl radical—is the most reactive compound among the carbonyl derivatives. The compounds below are shown in order of decreasing reactivity.





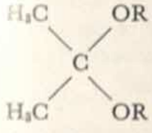
Some of the more significant addition reactions of the ketones are shown below; these reactions are analogous to those of the aldehydes.



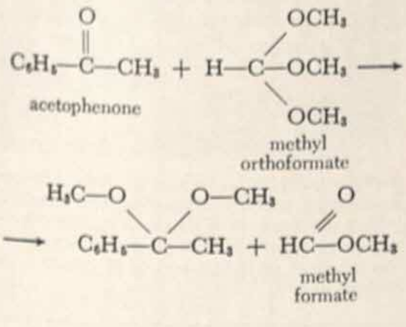


The addition products obtained with sodium bisulfite are characterized by a carbon-sulfur bond. They are crystalline solids that are often used in reactions to separate ketones from mixtures with other substances.

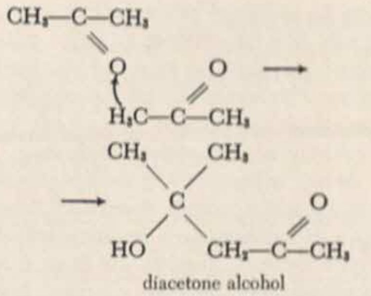
The reaction of alcohols with carbonyl compounds is considerably influenced by the steric factors mentioned above. Thus, although acetals can be obtained by a direct reaction of aldehydes with alcohols, the corresponding reaction will not succeed with ketones:


ketal of acetone

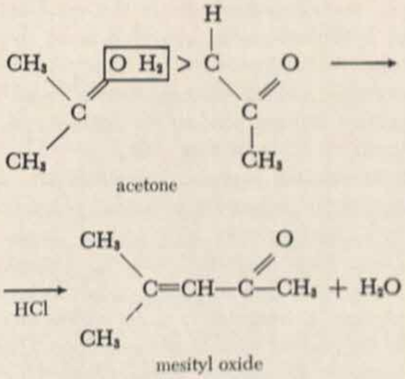
The ketals are prepared by reacting esters of orthoformic acid with acid catalysts, as shown below.



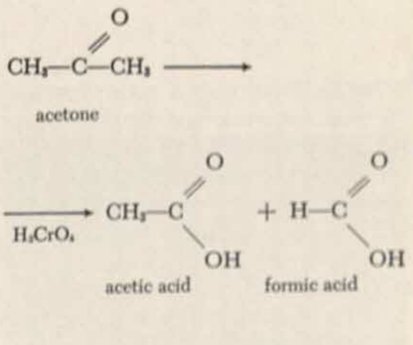
The aldol condensation reaction is not as favorable with ketones as with aldehydes. However, diacetone alcohol can be obtained from acetone in accordance with the reaction shown below.



Some ketones also condense in the presence of acid catalysts, with the elimination of water:



Unlike the aldehydes, ketones display considerable resistance to oxidizing agents. For this reason, they do not as readily reduce ammonia solutions of silver nitrate. Only by using strong oxidizing agents (such as chromic acid) can carboxylic acids be formed:



The reduction of a ketone leads to formation of the corresponding secondary alcohol. The reagents used are the same as those for the reduction of aldehydes to primary alcohols.

Grignard reagents react with ketones by adding to the $>C=O$ double bond. This is also analogous to their action with aldehydes. In this case, decomposition of the reaction product with water forms tertiary alcohols.

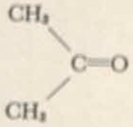
3

a

b

THE HYDRAZONE OF ACETOPHENONE—The condensations of the ketones with hydroxylamine, hydrazine, phenylhydrazine, and semicarbazide are analogous to those of the aldehydes. The resulting products are generally solids that can be easily crystallized, isolated and characterized as ketones. In Illustration 3a the various substances used to prepare a hydrazone are shown. The large watch glass contains a hydrochloride of hydrazine; the small watch glass contains sodium acetate. The small and large graduated cylinders contain, respectively, water and acetophenone. The beaker contains these four substances together. Illustration 3b shows the hydrazone obtained.

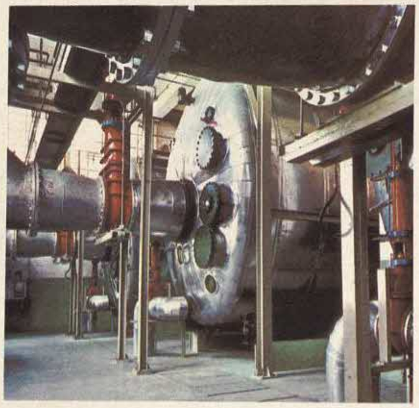
ACETONE



Acetone is a colorless liquid with a characteristic odor. It is highly volatile and is miscible in all proportions with water and the principal organic solvents.

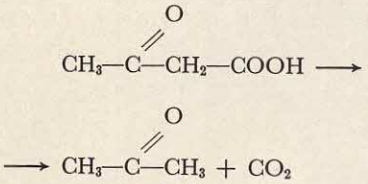
Traces of acetone are found in human blood and appreciable quantities are found in the urine of diabetics, where it

4



ACETONE RECOVERY—This illustration shows the section of a plant where acetone is recovered after its use in reacting with cellulose to prepare cellulose acetate.

is derived from acetoacetic acid:

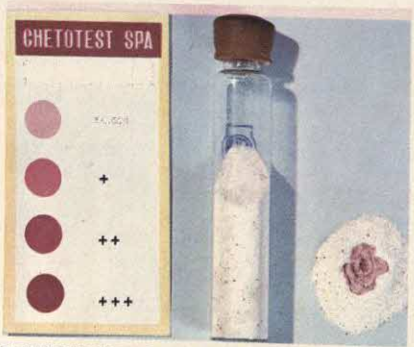


$$CH_3-\overset{O}{\overset{/\!/}{C}}-CH_2-COOH \longrightarrow$$

$$\longrightarrow CH_3-\overset{O}{\overset{/\!/}{C}}-CH_3 + CO_2$$

In addition to the two principal industrial methods of preparing acetone (heating calcium acetate, or passing acetic acid vapor over a heated catalyst), it can also be prepared by the fermentation of starch and the residues of sugar extraction (molasses) by means of microorganisms. This results in a mixture of acetone and other oxygenated compounds such as n-butyl alcohol and ethyl alcohol.

5

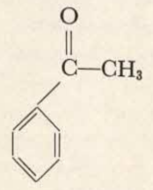


DETERMINATION OF THE ACETONE CONTENT OF URINE—Acetone is found in minimal quantities in normal human urine. More substantial quantities are found in the urine of diabetics and those suffering from liver infections. A method for determining abnormal levels of acetone consists of putting a few drops of the urine into the powder shown in the illustration and comparing the resulting color with those shown on the sample card. This analysis is possible because acetone in an alkaline environment—and in the presence of complex salts of heavy metals—takes on a coloration ranging from pink to deep purple, according to its concentration.

Many organic compounds—including natural and synthetic resins and derivatives of cellulose—are readily soluble in liquid ketones. Acetone and other members of the aliphatic ketone series (methyl ethyl ketone and methyl butyl ketone) are, therefore, used in the preparation of paints and as selective solvents. In certain industrial processes, for example, acetylene produced in the cracking of hydrocarbons is separated from the other reaction products by absorption in acetone. Acetone also represents an important starting product for organic synthesis on an industrial scale.

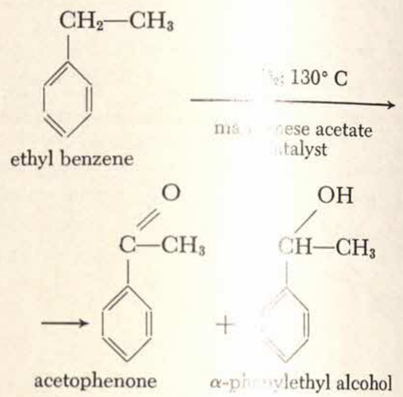
Among the acetone derivatives are a number of important industrial solvents with comparatively high boiling points. These include methyl isobutyl ketone, isophorone, and diacetone alcohol. Isophorone is insoluble in water and is one of the best solvents of nitrocellulose. The synthesis of methyl methacrylate (the methyl ester of methacrylic acid) from acetone has recently become of considerable industrial importance.

ACETOPHENONE



Acetophenone or phenyl methyl ketone—the most important and simplest representative of the mixed aliphatic-aromatic ketones—is a colorless liquid that is insoluble in water and that boils at 220° C (428° F). It is volatile in steam and has the composition $C_6H_5COCH_3$. Because of its anesthetic and soporific properties it has been used, under the name hypnone, to induce sleep. Acetophenone occurs to a small extent in coal tar.

Acetophenone is prepared industrially by direct oxidation (with air) of the corresponding hydrocarbon. This reaction is made possible by the effect that the aromatic ring has on the carbon atom being substituted:



The alcohol formed in this reaction can also be converted to acetophenone by dehydrogenation carried out at 200° C (392° F).

The Friedel-Crafts reaction is also applicable to acetophenone; for example, acetyl chloride with benzene yields acetophenone. This reaction is commonly considered as the process of uniting two or more organic molecules through the formation of carbon-to-carbon bonds under the influence of strong, acidic metal halide catalysts, such as aluminum chloride, boron fluoride, and so forth.

Acetophenone is also obtained by means analogous to the decomposition of cumene hydroperoxide in the industrial production of acetone and phenol.

Acetophenone is used as a solvent, as an ingredient of perfumes, as an aroma, and as an intermediate compound in organic synthesis.

6

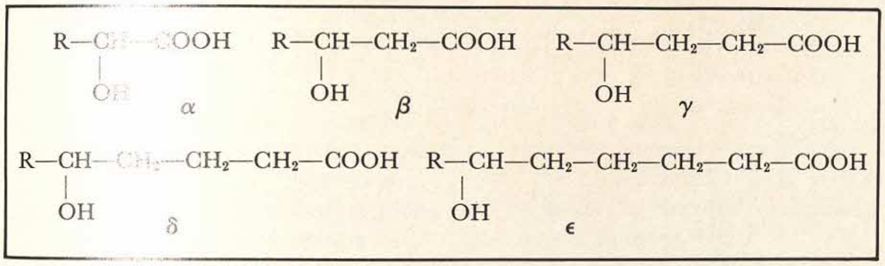
ANTHRAQUINONE—This cyclic ketone is prepared from phthalic anhydride and benzene, in the presence of a Lewis acid. *Ortho*-benzoylbenzoic acid is first obtained, which—in the presence of H_2SO_4 and heat—yields 9,10-anthraquinone.

THE OXYACIDS | hydroxyl and carboxyl in the same molecule

Oxyacid molecules are characterized by having both the hydroxyl group (−OH) and the carboxyl group (−COOH). These compounds are extremely reactive because they have the reactions characteristic of both of their component groups. This article considers the intramolecular reactions between acid and alcohol groups typically occurring in oxyacid compounds, and how these reactions serve to distinguish the various categories of oxyacids. Some of the aliphatic oxyacids are now recognized as being of considerable biological importance; as a result, much research in this particular field has been stimulated.

ALIPHATIC OXYACIDS

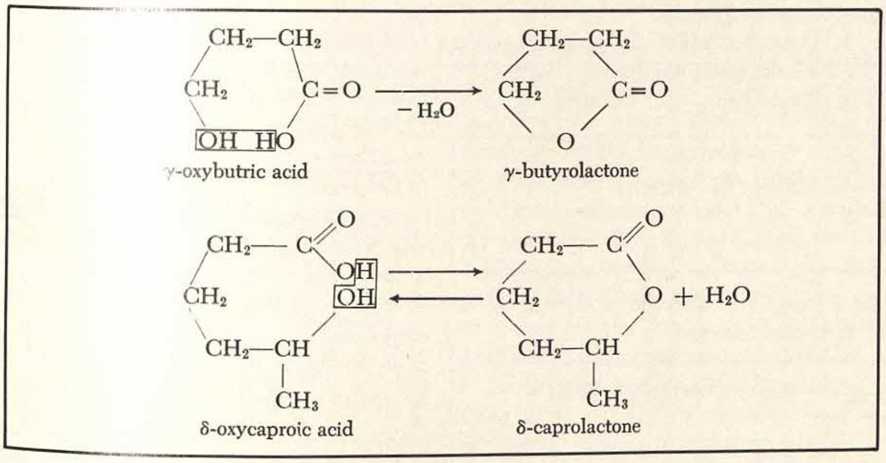
The character of intramolecular reactions is a function of the distance between the hydroxyl and carboxyl groups. The acids are thus classified by distance, as shown below.



$R{-}\underset{OH}{CH}{-}COOH$ α $R{-}\underset{OH}{CH}{-}CH_2{-}COOH$ β $R{-}\underset{OH}{CH}{-}CH_2{-}CH_2{-}COOH$ γ

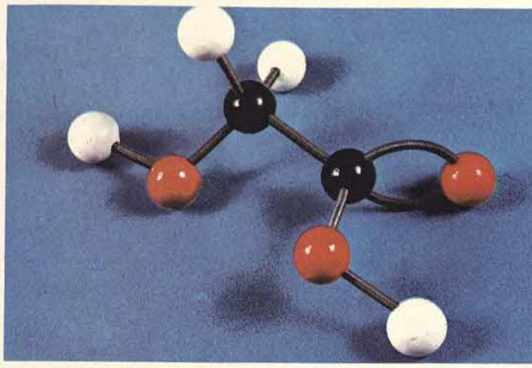
$R{-}\underset{OH}{CH}{-}CH_2{-}CH_2{-}CH_2{-}COOH$ δ $R{-}\underset{OH}{CH}{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}COOH$ ε

When heated the γ- and δ-acids undergo esterification. This reaction involves the elimination of water from the carboxyl and alcohol functions. Esters of the oxyacids (called lactones) are cyclic compounds having five or six carbon atoms, depending on whether they are derived from γ- or δ-oxyacids.



The most stable lactones are those with five-membered rings. These are formed quite easily, often by simply evaporating the aqueous solution of γ-oxycarboxylic acids. Syntheses suitable for the preparation of these acids often lead to the direct formation of the γ-lactones. Lactones with six-membered rings (δ-lactones) are not as stable and their rings open easily; even their formation reaction is an equilibrium reaction. The simpler γ- and δ-lactones are liquids soluble in water, alcohol, and ether. They can be distilled without decomposing. If boiled with water, the lactone rings open, yielding the corresponding oxyacids. Hydrolysis establishes lactone ⇄ oxyacid equilibrium. It is difficult, however, to form cyclic lac-

2



GLYCOLIC ACID—Glycolic acid is not an optically active compound. It is found in small quantities in the juice of sugar cane and sugar beet, in sour grapes, and in some leaves.

1

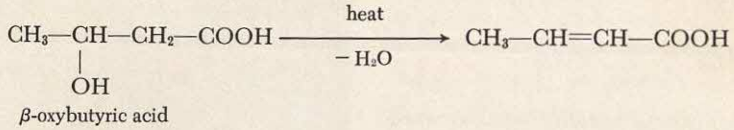
ANGELICA ARCHANGELICA—The oil found in the roots of *Angelica archangelica* contains a lactone with a ring consisting of 16 carbon atoms. This lactone can also be obtained by the oxidation of cyclopentadacanone. The illustration shows the plant as it is in autumn when it has gone to seed.

CREAM OF TARTAR—Cream of tartar, the acid potassium salt of dextrorotatory tartaric acid, is found in grape juice. The illustration shows the crusts deposited on the walls of a barrel during the fermentation of wine. These crusts are the principal source for the production of tartaric acid.

3

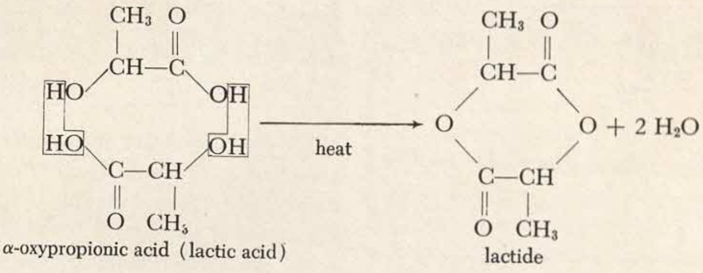
tones from ϵ-oxyacids. This is in agreement with the tendency to form cyclic compounds of five or six atoms in other classes of compounds.

The carboxyl-hydroxyl interaction in the case of other oxyacids yields products of a different character. The β-oxycarboxylic acids undergo dehydration into unsaturated acids, as shown in the following structure.


$$\mathrm{CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_2{-}COOH \xrightarrow[-H_2O]{\text{heat}} CH_3{-}CH{=}CH{-}COOH}$$

β-oxybutyric acid

The esterification reaction with α-oxyacids, on the other hand, involves two molecules of the oxyacid, as represented below:



α-oxypropionic acid (lactic acid)

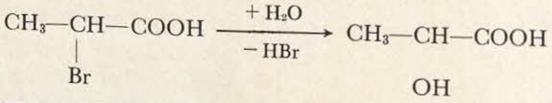
lactide

These reactions yield lactides, a name derived from the compound shown above. In a lactide, organic radicals may replace the two hydrogen atoms; or, hydrogen atoms may replace the two radicals. In the case of the latter reaction, the simplest lactide, glycollide, is produced.

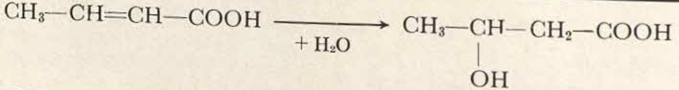
PREPARATION OF OXYACIDS

The two most general methods used to prepare oxyacids are:

1. The substitution of a hydroxyl group for the halogen in halogenated carboxylic acids by heating with water and alkalis.

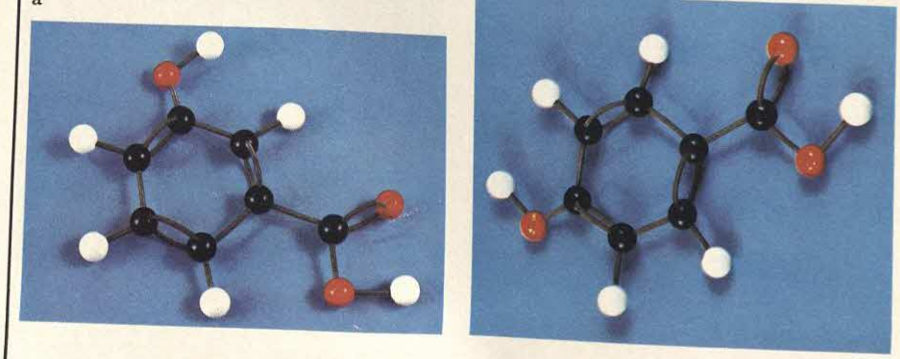

$$\mathrm{CH_3{-}\underset{\underset{\displaystyle Br}{|}}{CH}{-}COOH \xrightarrow[-HBr]{+H_2O} CH_3{-}\underset{\displaystyle OH}{CH}{-}COOH}$$

2. The addition of water to unsaturated carboxylic acids by heating with acids or alkalis. This method is shown in the following structure:


$$\mathrm{CH_3{-}CH{=}CH{-}COOH \xrightarrow[+H_2O]{} CH_3{-}\underset{\underset{\displaystyle OH}{|}}{CH}{-}CH_2{-}COOH}$$

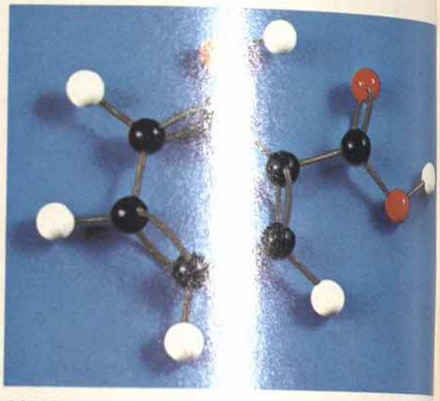
4

***META*-HYDROXYBENZOIC ACID AND *PARA*-HYDROXYBENZOIC ACID**—These two isomers (Illustrations 4a and 4b respectively) are less important than the *ortho* form. The *para*-isomer is formed in the course of the synthesis of salicylic acid.


a

b

5


SALICYLIC ACID—This is the most important aromatic oxyacid, and is used in aspirin. It is found in some plants, particularly in the leaves and flowers of *Gaultheria*, where it exists in the form of methyl esters.

Esters can also be prepared directly from carboxylic acids by reaction with alcohols with the loss of water. Sulfuric acid or hydrochloric acid is ordinarily used as a catalyst for this reaction. Since this is a reversible reaction, esters may be split by water to yield carboxylic acids. When alkaline hydrolysis is used, the process is referred to as saponification because the preparation of soap utilizes this process.

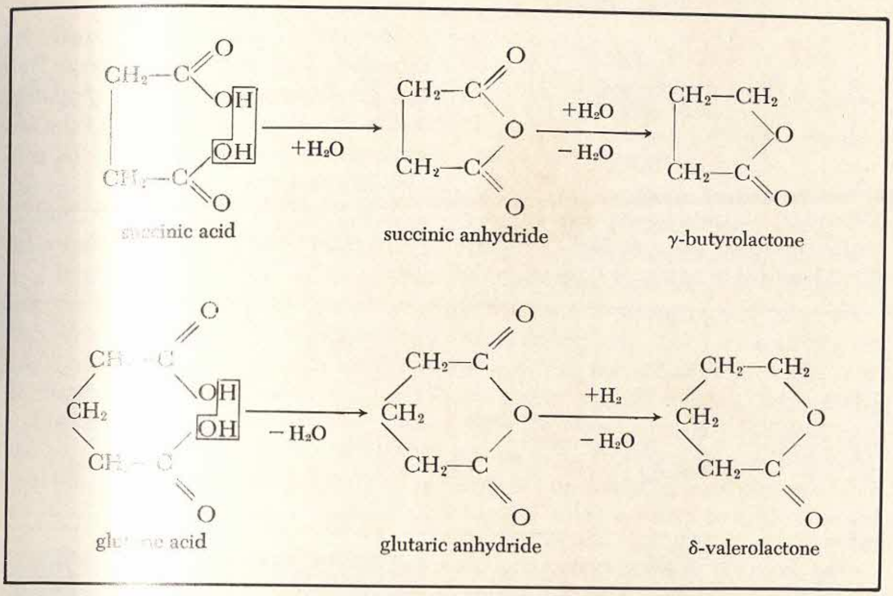
A number of substituted carboxylic acids are known. The halo acids are ordinarily made by direct halogenation of the carboxylic acid in the presence of a small amount of phosphorus trihalide.

Other methods suitable for particular classes of oxyacids are frequently used under laboratory conditions: the α-oxyacids can be obtained from aldehydes and ketones, via the hydrocyanines; the γ- and δ-lactones can be obtained from the corresponding dicar-

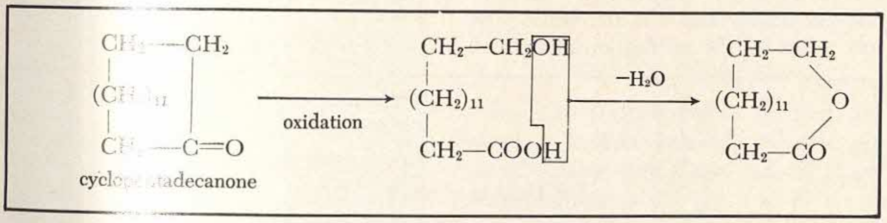
6

A LEMON TREE—Lemons that have not completely ripened contain large quantities of citric acid. Like all other citrus fruits—and fruits in general—lemons also contain vitamin C (ascorbic acid).

boxylic acids by reduction with sodium and alcohol (see below).



Lactones of larger ring size are relatively more stable. An interesting preparation of macrocyclic lactones results when the corresponding cyclic ketones are oxidized. The chemical structure for this reaction is shown below.



Some lactones of this type are found in nature; they have the smell of moss.

GLYCOLIC ACID ($CH_2OH-COOH$)

Glycolic acid—the simplest of the aliphatic oxyacids—is obtained in the laboratory by boiling an aqueous solution of potassium chloroacetate:

$$Cl-CH_2-COOK + H_2O \rightarrow HO-CH_2-COOH + KCl.$$

Glycolic acid is a white crystalline solid that melts at 79 to 80° C (about 174 to 176° F). Its industrial applications include textile printing, leather tanning, and magnetic plastics. The most recently introduced industrial preparation reacts formaldehyde, carbon monoxide, and water at 300 atmospheres on acid catalysts:

$$H-C-HO + CO + H_2O \rightarrow CH_2OH-COOH.$$

LACTIC ACID ($CH_3-\overset{*}{C}HOH-COOH$)

Lactic or α-oxypropionic acid is made by the scission of carbohydrates by certain bacteria. This is why it is found in such products as sour milk, wine, and cheese.

The carbon atom indicated by the asterisk in the formula is asymmetric. Lactic acid, therefore, exists in two optically active forms. Normal methods of synthesis yield an equimolecular mixture of both enantiomers. This mixture is a colorless and viscous liquid at ordinary temperatures. The *d* and *l* forms, on the other hand, are crystalline solids that melt at 52.8° C (about 127° F) and are prepared by the fermentation of carbohydrates (saccharose and maltose).

Lactic acid is synthesized industrially from aldehydes via hydrocyanine, and by the fermentation of carbohydrates. The fermentation process normally uses the *Lactobacillus delbrückii,* a species of bacteria that becomes optically active at 50° C (122° F), and at a pH between 5.0 and 5.5, preferably in the presence of suitable material and protein compounds and an excess of calcium carbonate. The calcium carbonate neutralizes the lactic acid formed in the process, thereby avoiding an excessive lowering of the pH and consequent cessation of the fermentation.

Lactic acid is used in the tanning industry for controlling the acidity of vegetable tanning liquors, for deliming hides, and as a plumping and drenching agent. It is used in the acid dyeing and printing of wool and as a flavoring agent and preservative in processed cheese, salad dressing, pickles, and carbonated beverages. Other uses include the preparation of lactates, organic solvents, pharmaceuticals, and cosmetics, the softening of waters used in brewing and other processes, and fermentation control in the drying of egg white and in the purification and processing of gelatins and pectin from apple pomace.

For some needs lactic acid may be used alternately with other acids such as tartaric and citric. It has also been used—experimentally—to produce plastics and elastomers.

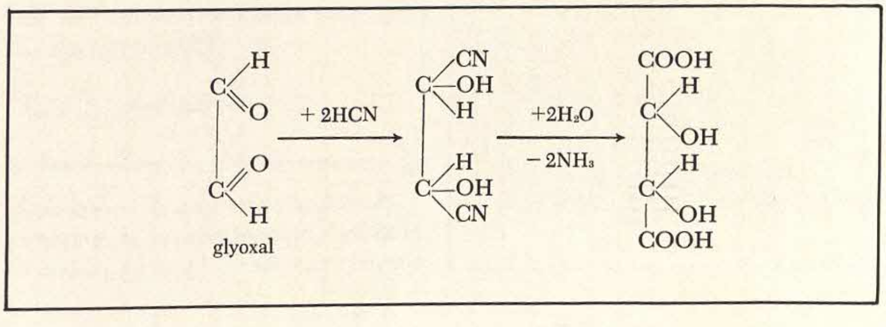
TARTARIC ACID

($COOH-\overset{*}{C}HOH-\overset{*}{C}HOH-COOH$)

This important dicarboxylic oxyacid contains two asymmetric carbon atoms (indicated by asterisks). Thus, four isomeric forms are possible. Two of these exist as nonsuperimposable mirror images of one another; the other two are intact, identical, and optically active (meso) by virtue of their having a plane of symmetry.

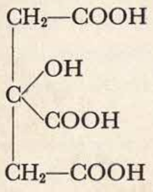
The dextrorotatory form is found in numerous plants and fruits. It is a white crystalline solid that fuses at 169 to 170° C (about 336 to 338° F). The levorotatory acid has the same physical and chemical properties as the dextrorotatory form. It is far less abundant in nature, however, and is found primarily in the leaves and fruit of *Bauhinia reticulata* (an African plant).

Racemic tartaric acid (a 1:1 mixture of the dextrorotatory and levrorotatory forms) melts at 205 to 206° C (about 401 to 403° F), the highest melting point of all the forms. Pasteur used this substance in his studies on the separation of racemic mixtures. This form of tartaric acid is obtained by an extension of the synthesis via hydrocyanine.



Tartaric acid is used in the food industry, the textile industry, galvanoplastics, and photography. Cream of tartar (potassium bitartrate) is used to prepare the acid and as a food ingredient. Tartar emetic (antimonyl potassium tartrate) is used as an emetic, as a mordant, and in the treatment of tropical infections such as schistosomiasis. The emetic is given intravenously; concentrations above 0.5 percent are poorly tolerated.

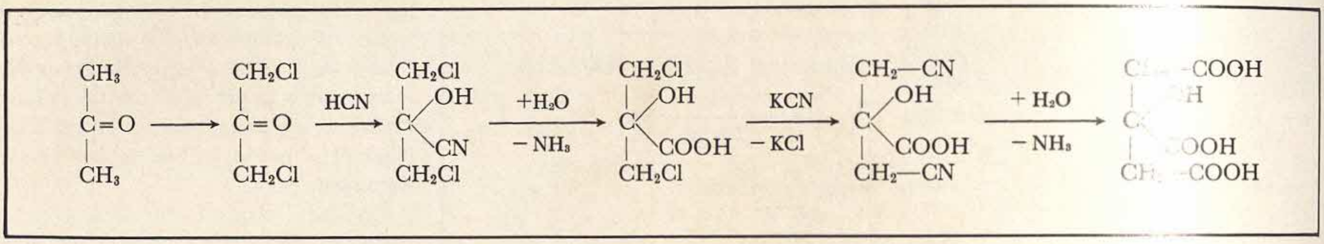
CITRIC ACID



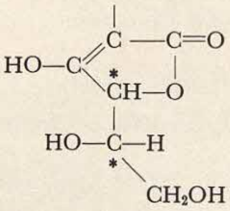
Citric acid, a tricarboxylic oxyacid, is a white solid that melts at 153° C (307.4° F). Abundant in nature, it is found in the juice of lemons and other fruits such as currants.

The acid is prepared industrially by extraction from the juice of unripe lemons. This is usually done by precipitation in the form of calcium salts and the fermentation of the carbohydrates by suitable agents (citromycetes).

A synthesis of essentially theoretical interest begins with acetone, as shown below.



ASCORBIC ACID

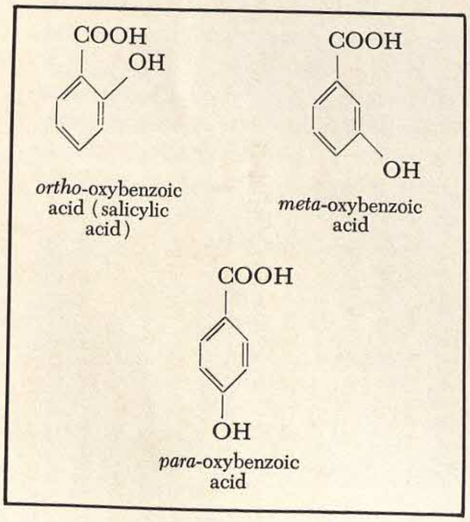


Ascorbic acid—better known as vitamin C—is needed to prevent scurvy. The lactonic form (shown above) has a chemical structure similar to the carbohydrate. Ascorbic acid is obtained industrially from L-sorbose, a sugar containing six carbon atoms. This sugar is found in fresh fruits and vegetables.

The biologically active product, which has vast applications in medicine, is the optically active *l*-form.

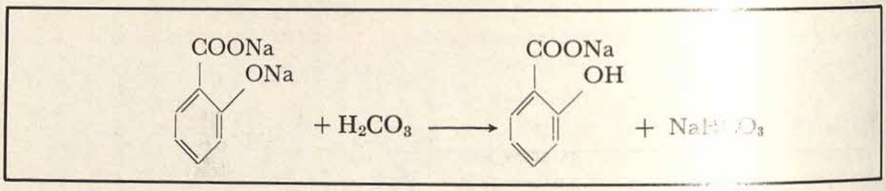
AROMATIC OXYACIDS

The three fundamental compounds in this category are shown below.



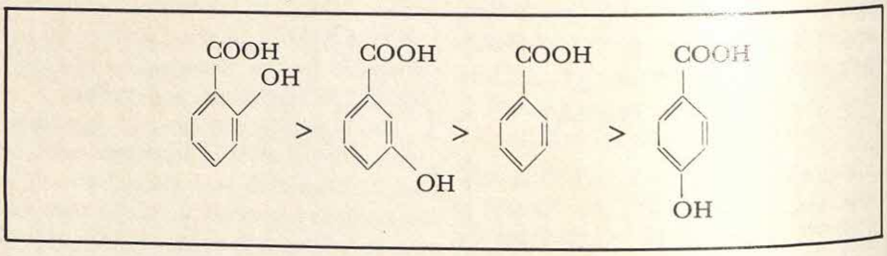
The hydroxyl in these compounds has a phenolic, rather than an alcoholic, character. This is due to the fact that it is connected to an aromatic nucleus. The phenolic hydroxyl is characterized by its greater acidity and it is, therefore, possible to obtain the salification of both the hydroxyls—phenolic and carboxylic—by the action of an excess of caustic alkalis.

The acidity of the phenolic hydroxyl, however, is less than that of the carboxyl. This is illustrated by the reaction shown below.



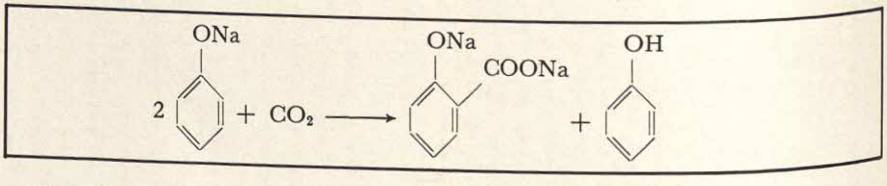
In the reaction just described, the carbonic acid—a weak acid—succeeds in removing the metal only from the phenolic hydroxyl.

The acidity of the carboxyl is increased when the hydroxyl is in the *ortho*-position; it is diminished when it is in the *para*-position. The relative acidities are shown below.



SALICYLIC ACID

Salicylic—or *ortho*-hydroxybenzoic—acid is the most important of the aromatic oxyacids because of its use in pharmaceuticals and foodstuffs and because of its many derivatives. It is a crystalline solid that melts at 158° C (316.4° F). It is prepared by reacting dry sodium phenate and carbon dioxide. In this process—called Kolbe's synthesis, after the German chemist Adolph Kolbe who first developed it—the reaction takes place at 180 to 200° C (356 to 392° F):



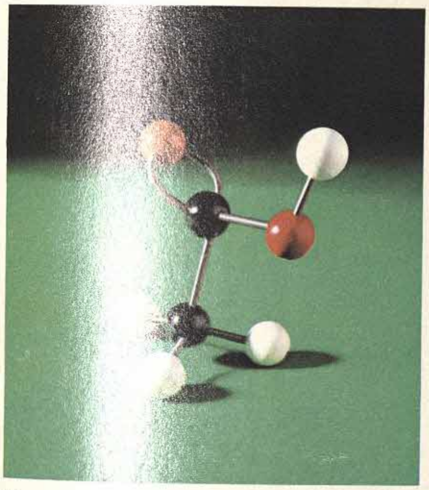
The Schmitt process is an improvement of Kolbe's original process. It completely converts the phenol by using carbon dioxide under pressure (at four to seven atmospheres) at a temperature of 120 to 140° C (248 to 284° F).

CARBOXYLIC ACIDS | chemical characteristics and processing methods

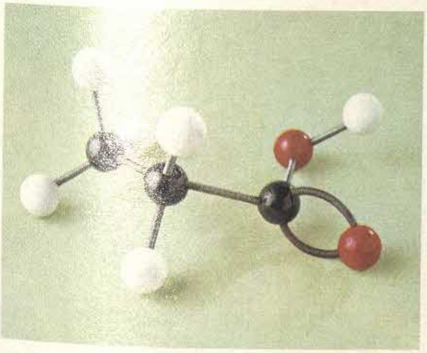
Anyone who has ever suffered from a mosquito bite or a bee sting should know that these insects have the ability to inject formic acid into the bodies of their adversaries. This acid, the simplest of the organic acids, also forms the basis for a host of compounds from fertilizers to plastics.

The hydrogen ion, or proton, performs the acid function in chemistry, and it is the carboxyl group that provides the proton in organic chemistry. The general formula for the carboxylic acids is RCOOH, where R is any organic radical. Thus, acetic acid is CH_3COOH.

1a

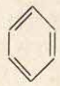


1b

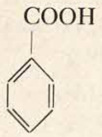


ACETIC AND PROPIONIC ACIDS—These two acids, represented here by their molecular structures (Illustrations 1a and 1b, respectively), are among the first members of the carboxylic acid series. Both are of industrial importance.

The list of carboxylic acids is quite long, and the compounds contain from one to 25 or more carbon atoms. A system for naming these acids has been adopted internationally. Simply, the name of the corresponding hydrocarbon is changed by dropping the final -e and substituting -oic. Formic acid, for example, has only one carbon atom in its molecule and corresponds to methane; thus, its official name is methanoic acid. Acetic acid, corresponding to ethane, becomes ethanoic acid, and so forth. Carboxylic acids are also formed from the aromatic series of hydrocarbons, with the same rules for naming. For example,



benzene



benzoic acid

The carboxylic acids of greatest importance to the chemical industry are those with relatively few carbon atoms per molecule:

$HCOOH$
formic acid (methanoic)

CH_3COOH
acetic acid (ethanoic)

CH_3CH_2COOH
propionic acid (propanoic)

$CH_3CH_2CH_2COOH$
butyric acid (butanoic)

As the number of carbon atoms increases, the higher forms of the series derive their importance from the fact that they occur in the natural fats. Two examples are:

$CH_3(CH_2)_{14}COOH$
palmitic acid

$CH_3(CH_2)_{16}COOH$
stearic acid

Both of these acids are prime ingredients in soap manufacture.

CHEMICAL PROPERTIES

In the functional $-COOH$ group of the carboxylic acids, the oxidation state of carbon atoms reaches its maximum level in organic molecules. Ethane, CH_3CH_3, when gradually oxidized, yields the following products in the process:

$$\underset{\text{ethane}}{CH_3CH_3} \rightarrow \underset{\text{ethyl alcohol}}{CH_3CH_2OH}$$

$$\rightarrow \underset{\substack{\text{acetal-}\\ \text{dehyde}}}{CH_3CHO} \rightarrow \underset{\text{acetic acid}}{CH_3COOH}$$

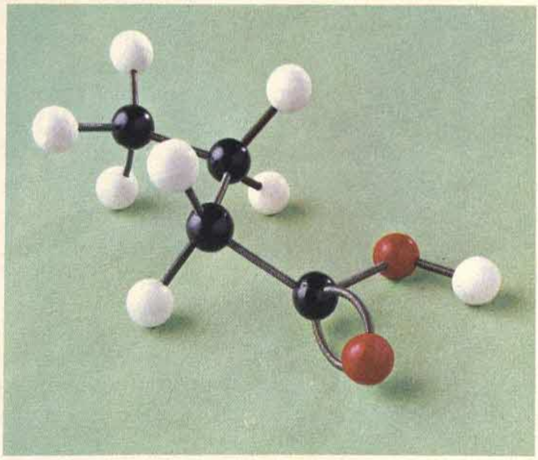
The degree of acidity of these organic acids is considerably less than that of their inorganic counterparts. Acetic acid, one of the strongest acids in the series, dissociates to less than 0.000001 the extent of hydrochloric acid; that is, like the mineral acids, organic acids dissociate into hydrogen ions and negative ions in water, but to a much lesser extent than mineral acids. The ionization of acetic acid, $CH_3COOH \rightarrow CH_3COO^- + H^+$, demonstrates that a hydrogen ion is available for replacement by metals. Reacting the acid with a base results in the formation of a true salt:

$$CH_3COOH + NaOH$$
$$\rightarrow CH_3COONa + H_2O.$$

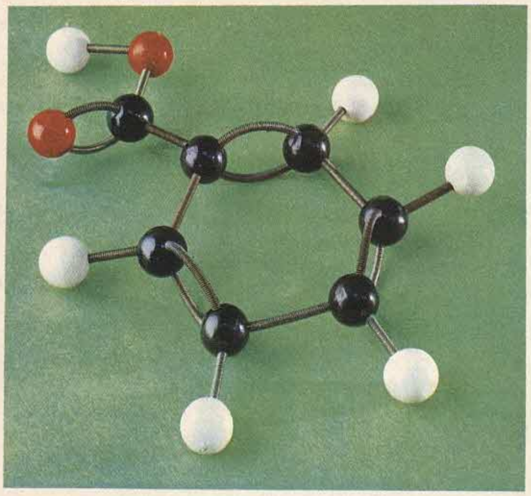
The $-OH$ portion of the carboxyl group is capable of producing various com-

BUTYRIC ACID—This acid is important chemically; it is found in nature only in the milk of mammals. It is also responsible for the distinctive odor of rancid butter.

2



3



BENZOIC ACID—Cyclic compounds are also used to produce carboxylic acids. These compounds, sometimes called aromatic acids, are made by substituting carboxyl groups for the hydrogen atoms of aromatic nuclei. Illustration 3 is a representation of the benzoic acid molecule.

pounds by substitution reactions. If, for instance, a reaction takes place with phosphorus halides (PCl_3, PBr_3, PI_3, for example), the products are the chlorides, CH_3COCl; bromides, CH_3COBr; and iodides, CH_3COI, respectively, of the acids. These compounds are highly reactive, thus enabling the replacement of the halogen with other groups (which may include another halogen).

When combined with alcohols, in the presence of a strong proton donor, the organic acids produce a class of compounds known as esters:

$$\underset{\text{acetic acid}}{CH_3COOH} + \underset{\text{ethanol}}{CH_3CH_2OH}$$

$$\rightarrow \underset{\text{ethyl acetate}}{CH_3COOCH_2CH_3} + H_2O$$

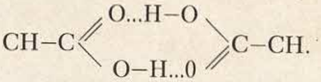
These compounds are found widely in nature and are of great industrial importance. Esters of the higher fatty acids in combination with glycerol form natural fats—essential components of both the animal and vegetable kingdoms.

PHYSICAL PROPERTIES

Depending on the number of carbon atoms in the molecule, the organic acids are either liquid or solid at normal temperatures. The first compounds in the series are easily soluble in water, a property not possessed by the higher members. In addition, the liquid acids, such as formic, acetic, and butyric, have pungent, irritating odors. Vinegar is a dilute solution of acetic acid, and butyric acid is responsible for the disagreeable odor of rancid butter.

As the number of carbon atoms increases, the acids become less and less soluble until a point of insolubility is reached wherein 17 carbon atoms exist in the molecule. This phenomenon is due to the fact that the polar effect of the carboxyl group, which gives the acid its solubility factor, is unable to match the nonpolarity of the hydrocarbon chain.

The carboxyl group is also responsible for the ability of the acid molecules to unite in pairs by hydrogen bonding (association):



(The dotted lines represent the hydrogen bonds.) This property is common to many types of compounds—water and alcohols, for example—and gives rise to great differences in a physical constant such as the boiling point. This is clearly illustrated in comparing an ether, an alcohol, and an acid, each with an identical number of carbon atoms:

CH_3OCH_3
dimethyl ether
b.p. −23.6° C
(−10.48° F)

CH_3CH_2OH
ethyl alcohol
b.p. 78°C (172.4°F)

CH_3COOH
acetic acid
b.p. 118° C (244.4° F)

The boiling point of the ethers is considerably lower than in the other classes of compounds because of the lack of hydrogen bonds.

PROCESSING

Because the carbon atom is near its maximum oxidation state in the carboxylic acids, a practical method of production is to oxidize alcohols or aldehydes. The latter compounds, because they are at a relatively lower state of oxidation, readily convert to the acids. Formaldehyde, for example, yields formic acid directly in the presence of oxygen, and acetaldehyde forms acetic acid in a similar manner:

$$H{-}CHO \xrightarrow{O} H{-}COOH$$

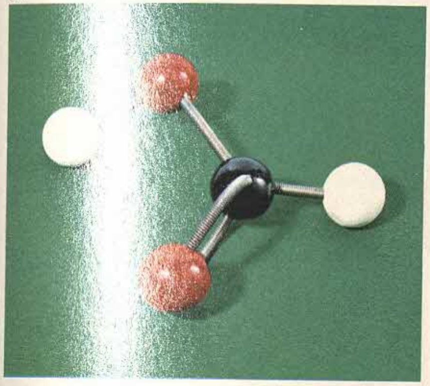
$$CH_3CHO \xrightarrow{O} CH_3COOH$$

To produce the acids, oxidation is carried out with oxygen and catalysts, which increase the speed and efficiency of the reaction. On a smaller scale, chemical oxidizers such as potassium permanganate or nitric acid are used. In the manufacture of acetic acid, still another method is employed. Here, oxidation of an alcohol is obtained using microorganisms (*Mycoderma aceti,* also called

4

***ACETOBACTER ACETI*, A NATURAL OXIDIZER**—In certain instances, as with acetic acid, carboxylic acids can be produced by oxidizing alcohols with microorganisms. Illustration 4 is a photomicrograph of these organisms (*Acetobacter aceti*). Chemically, acetic acid is produced by oxidizing acetaldehyde in the presence of catalysts. It can also be obtained in pure form from lower hydrocarbons. (1,300 X)

5a



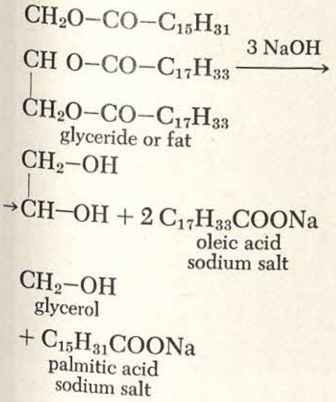
FORMIC ACID—Illustration 5a is a model of this acid's molecular structure. Formic acid is the simplest of carboxylic acids, and is the first in the series. It owes its name to the red ant, *Formica rufa,* shown in Illustration 5b.

"mother of vinegar"). These microorganisms release enzymes that are capable of transforming alcohol into acid:

$$CH_3CH_2OH \xrightarrow[\text{enzyme}]{O} CH_3COOH + H_2O.$$

Another common production technique, especially for making long-chain carboxylic acids, is the saponification of fats and oils. Fats and oils are esters of the "fatty" acids in combination with glycerol, and their molecular weights are on the high end of the scale. When these compounds are treated with steam or by chemical means, saponification occurs.

The resultant products are glycerol and a mixture of fatty acids (as their sodium salts):

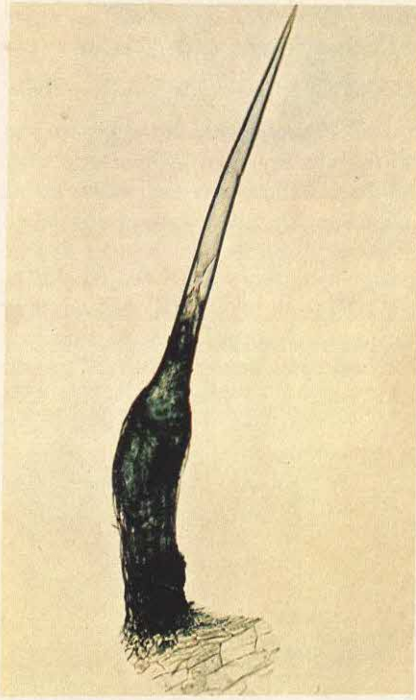


$$\begin{array}{l} CH_2O-CO-C_{15}H_{31} \\ CH\ O-CO-C_{17}H_{33} \xrightarrow{3\,NaOH} \\ | \\ CH_2O-CO-C_{17}H_{33} \\ \quad \text{glyceride or fat} \\ CH_2-OH \\ | \\ \rightarrow CH-OH + 2\,C_{17}H_{33}COONa \\ \qquad\qquad\qquad \text{oleic acid sodium salt} \\ CH_2-OH \\ \quad \text{glycerol} \\ + C_{15}H_{31}COONa \\ \quad \text{palmitic acid sodium salt} \end{array}$$

5b

The sting of mosquitoes and bees is the result of this acid being injected under the skin. Certain plants also contain this acid, among them the nettle family and some pines.

5c

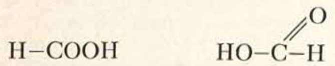


Still another method for acid production is to oxidize saturated hydrocarbons. However, this reaction has its limitations since it yields a mixture of acids that are difficult to separate from one another. In addition, the reaction does not respond easily to control and is difficult to stop at the desired point of oxidation. Finally, intermingled with the acid products are unwanted aldehydes and ketones. Nonetheless, successful attempts have been made to obtain the medium and higher weight fatty acids (palmitic and stearic acids, for example) from commercial paraffin, itself a mixture of higher hydrocarbons. Of economic interest is continuing research to find ways to convert paraffins into fatty acids through oxidation. This problem is directly linked with the still more important goal of producing fats from petroleum.

FORMIC ACID $H-COOH$

Formic acid takes its name from the red ant (*Formica rufa*), which is able to produce the compound as a free acid. The chemical has been known since the seventeenth century, and in the past has been produced by digesting the ants in water and distilling the resulting solution. The hairs of the nettle plant and some pine needles also contain the acid; hence, the irritation to skin on contact. Traces of formic acid are also found in human muscle and blood tissues.

The acid, simplest of the carboxylic acids, contains two functions: the carboxyl ($-COOH$) and the aldehyde ($-CHO$). These are represented in formic acid and formaldehyde:



$$H-COOH \qquad HO-\overset{\overset{O}{/\!\!/}}{C}-H$$

Thus, this compound has properties shared by no other acid in the series. It has, for example, reducing properties characteristic of the $-CHO$ group, and like the aldehydes possesses antiseptic properties. Industrial production methods begin with sodium hydroxide and carbon monoxide:

$$NaOH + CO \xrightarrow{120\text{–}150°\ C} HCOONa.$$

The sodium formate is then treated with sulfuric acid to liberate the formic acid.

Formaldehyde, $H-CHO$, is obtained in large quantities from methane, and can also be used to produce formic acid. Because of its relatively low cost, this acid is used commercially in the textile industry. Formaldehyde is used widely in the manufacture of plastics. It is also used as an embalming agent and as a sterilizing agent for soil.

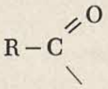
DERIVATIVES OF CARBOXYLIC ACIDS

the acyl group that gives rise to many families

The most widely distributed and abundant of all elements, carbon is a constituent of all organic matter. In fact, organic chemistry is the study of the compounds of carbon. The carboxylic acids are among the more important carbon compounds.

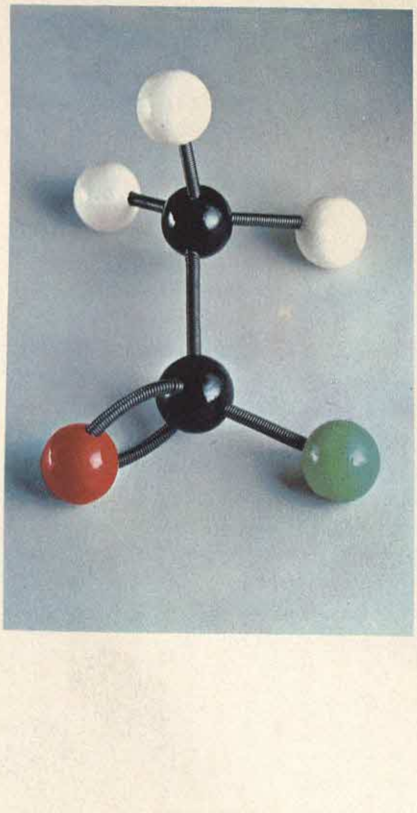
Derivatives of the carboxylic acids form the basis of some of the most common substances known to man—aspirin, vinegar, and essential oils, to name a few. Such derivatives are commonly used in the manufacture of textiles, plastics, drugs, and paper.

Actually, many compounds can be considered to be derived from the carboxylic acids—the chlorides, the anhydrides, the amides, and the esters. All of these contain the acyl group



and are obtained by interchange of the —OH and various other groups such as the CO group.

MOLECULAR MODEL OF ACETYL CHLORIDE —Acyl chlorides are made from corresponding acids reacting with thionyl chloride, phosphorus trichloride, or phosphorus pentachloride. In this model, the black spheres represent carbon, white hydrogen, red oxygen, and green chlorine.



Some of the important compounds formed in this way are acetyl chloride, CH_3COCl, and acetic anhydride, $(CH_3CO)_2O$, both used in industry and the laboratory; and the amides and nitriles, many of them contained in pharmaceuticals.

HALIDES AND ANHYDRIDES

Acid halides are substances in which the hydroxyl group of the acid has been replaced by a halogen atom. For example, acetic acid reacts with phosphorus halides to form acetyl chloride, CH_3COCl; acetyl bromide, CH_3COBr; and acetyl iodide, CH_3COI:

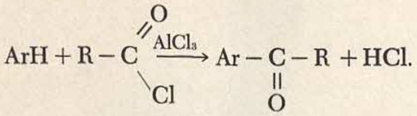
$$CH_3COOH + PCl_3 \rightarrow CH_3COCl + POCl + HCl.$$

These compounds decompose in water to form carboxylic acids:

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl.$$

In fact, if acetyl chloride is exposed to air, it emits fumes of hydrochloric acid.

All acid halides have low boiling points and are highly reactive; the halogen can be easily substituted by the most diverse groups, including $-OH$, $-OC_2H_5$, $-NH_2$, $-NHOH$, and $-NHNH_2$. Indeed their importance is largely due to this fact. They also can be used to introduce the acid radical into other compounds. One general example (the Friedel-Crafts acylation) is:



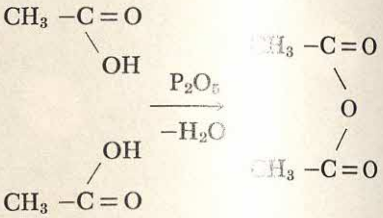
Acid halides thus react with water to form carboxylic acids, with alcohols to form esters, and with amines to form amides. Consider, for example, the case of acetyl chloride:

$$CH_3COCl + H_2O \rightarrow CH_3COOH + HCl \text{ hydrolysis}$$

$$CH_3COCl + C_2H_5OH \rightarrow CH_3COOC_2H_5 + HCl \text{ alcoholysis}$$

$$CH_3COCl + NH_3 \rightarrow CH_3CONH_2 + HCl \text{ ammonolysis}$$

Anhydrides constitute a class of compounds with a reactivity similar to that of the halides. They are formed by eliminating one water molecule from two molecules of the acid:

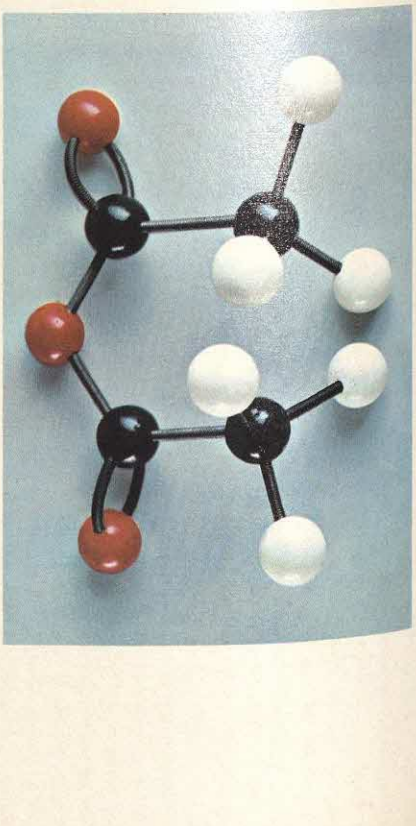


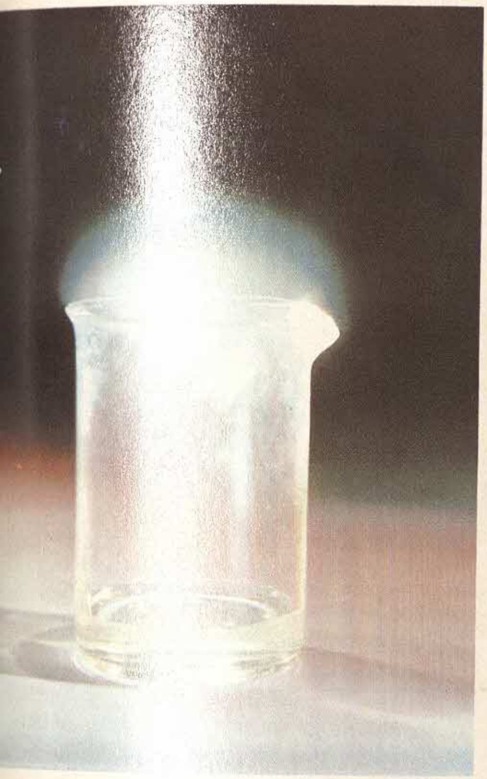
acetic acid

acetic anhydride

Formic acid, which causes painful wounds if it is allowed to come in contact with the skin, is an exception to this rule; its dehydration yields carbon monoxide. The first anhydrides in the series (up to C_{12}) are liquids, which have higher boiling points and greater molecular weights (almost double) than those of the acids. Anhydrides are made by reacting a molecule of sodium salt with a halide molecule

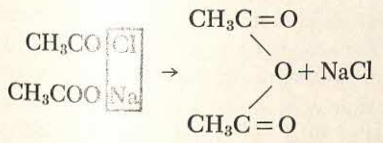
MOLECULAR MODEL OF ACETIC ANHYDRIDE —Acetic anhydride, the most common of anhydrides, is prepared from acetone, which decomposes into methane and ketene when heated. Ketene then reacts with a molecule of acetic acid to form the anhydride. The reaction is similar to that of the acyl chlorides, but takes place much more slowly.



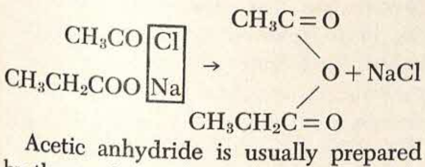


FUMES OF HYDROCHLORIC ACID—Acetyl chloride reacts with water to form acetic and hydrochloric acids, the latter visible as fumes when brought into contact with air.

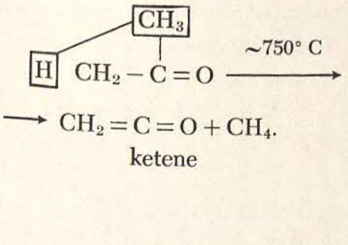
of the same or different acid:



Mixed anhydrides are also obtained by using radicals of different acids. A molecule of acetyl chloride thus reacts with a molecule of sodium proprionate to form acetyl propionic anhydride:



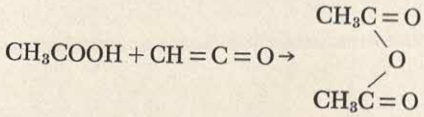
Acetic anhydride is usually prepared by the cracking of acetone, which results in the formation of ketene:



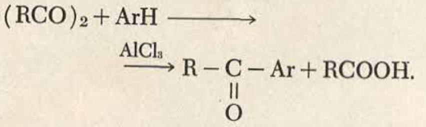
$$\boxed{H}\ CH_2-\overset{\boxed{CH_3}}{\overset{|}{C}}=O \xrightarrow{\sim 750°\ C} CH_2=C=O+CH_4.$$

$$\underset{\text{ketene}}{CH_2=C=O}$$

Ketene is then made to react with acetic acid to obtain the anhydride:



Organic chemistry makes frequent use of the simpler anhydrides, in addition to the acid halides, to introduce the acid radical (acylation):



$$(RCO)_2+ArH \longrightarrow \xrightarrow{AlCl_3} R-\underset{\underset{O}{||}}{C}-Ar+RCOOH.$$

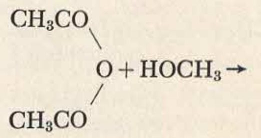
Anhydrides react with boiling water to yield acids:

$$(CH_3CO)_2O+H_2O \rightarrow 2CH_3COOH,$$

with ammonia to form amides

$$(CH_3CO)_2O+2NH_3 \rightarrow \underset{\text{acetamide}}{CH_3CONH_2}+\underset{\text{ammonium acetate}}{CH_3COONH_4},$$

and with alcohols as follows:



$$\rightarrow \underset{\text{methyl acetate}}{CH_3COOCH_3}+\underset{\text{acetic acid}}{CH_3COOH} \rightarrow$$

Acylation may be defined as the substitution of a hydrogen atom by the acyl group. Acetylation differs from acylation in that a hydrogen atom of a hydroxyl group is replaced by the acyl group. In the human body, this reaction is very important biologically, for it constitutes one stage in the intermediate metabolism of fats and sugars. Acetylation also has extremely important industrial applications, as in vinyl acetate (plastics and resins), ethyl acetate (solvents), and acetyl salicylic acid (aspirin).

Acetyl cellulose, used in the manufacture of such synthetic fibers as rayon acetate, is a special example of acetylation. Chemically a polytrivalent alcohol, cellulose can be treated to obtain monoesters, diesters and triesters. Cloth made of fibers of cellulose triacetate is practically wrinkle-free.

AMIDES AND NITRILES

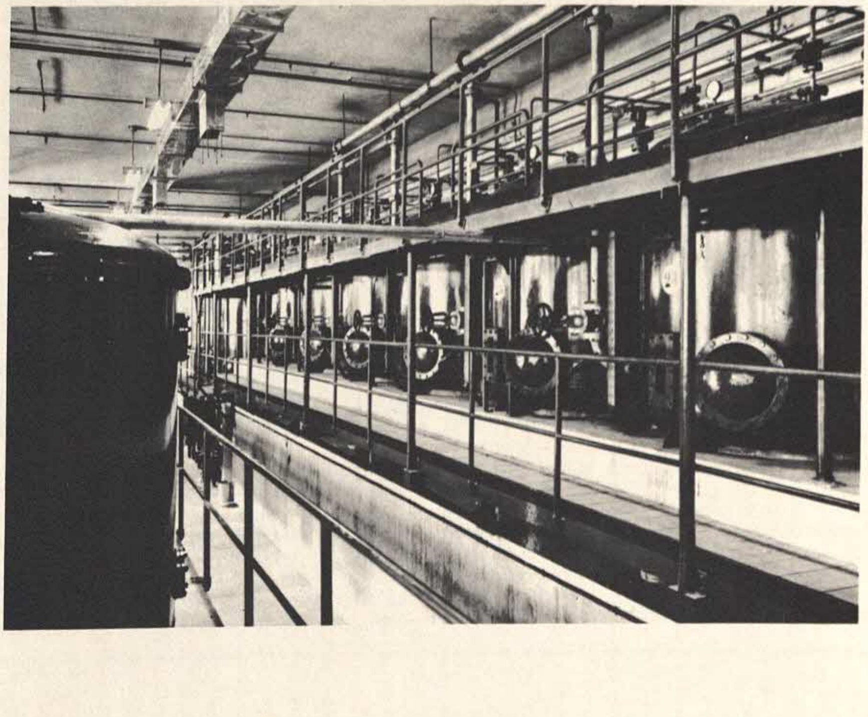
Amides are obtained by treating the chlorides, anhydrides, or esters of acids with ammonia:

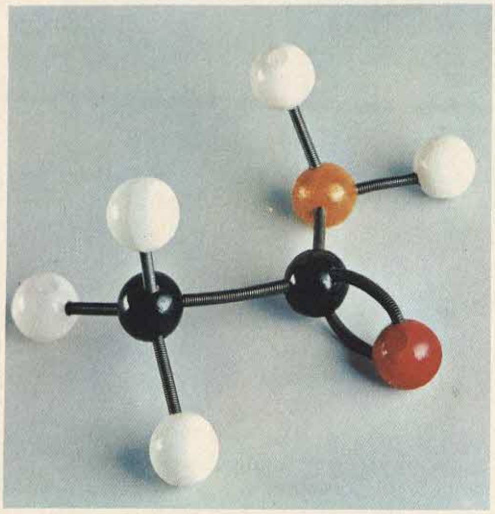
$$CH_3COCl+2NH_3 \rightarrow CH_3CONH_2+NH_4Cl$$

$$(CH_3CO)_2O+2NH_3 \rightarrow CH_3CONH_2+CH_3COONH_4$$

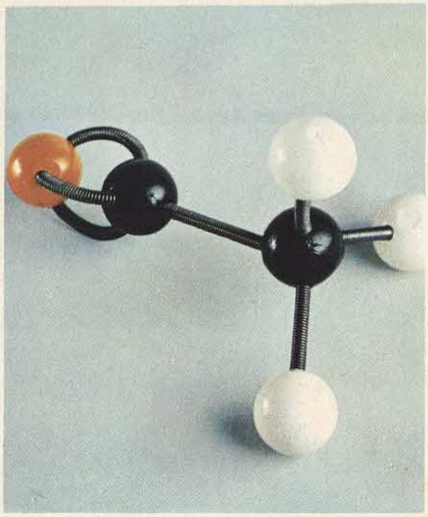
$$CH_3COOCH_2CH_3+NH_3 \rightarrow CH_3CONH_2+CH_3CH_2OH$$

PRODUCTION OF CELLULOSE ACETATE—Industrial production of cellulose acetate takes place in modern filtering rooms like this one. Raw cellulose reacts with acetic anhydride in the presence of sulfuric acid (catalyst) and diluents. One well-known end product is the familiar rayon acetate. Cellulose acetate is also used for photographic film.

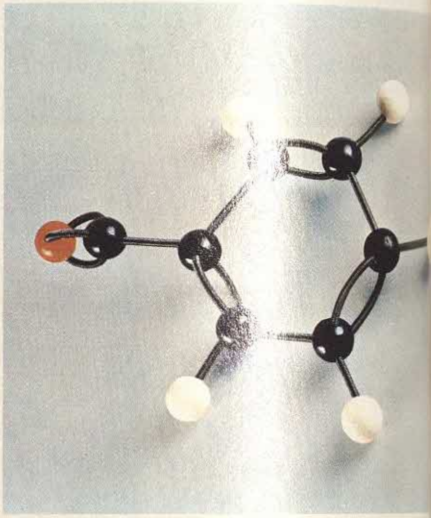




ACETAMIDE—Amides are generally prepared from acid chlorides and ammonia, or from carboxylic acids and ammonia. In this model, the acetamide has the formula CH_3CONH_2; the orange sphere represents a nitrogen atom.



ACETONITRILE—Nitriles are prepared by heating alkyl halides with sodium cyanide in a solvent capable of dissolving both substances. Acids are obtained from the nitriles by hydrolysis (acid or base).



EXPANDED MOLECULAR MODEL OF BENZONITRILE—Nitriles are considered to be derivatives of prussic acid, from which they are obtained by substituting the hydrogen atom with an organic radical. Benzonitrile is an aromatic nitrile.

Amides are prepared in the laboratory by the first two methods; they are made industrially from the ammonium salts of carboxylic acids:

$$RCOOH + NH_3 \rightarrow RCOO^-NH_4^+ \xrightarrow{heat} RCONH_2 + H_2O.$$

When heated with aqueous solutions of acids or bases, amides hydrolyze to form free acid:

$$CH_3CONH_2 + H_2SO_4 + H_2O \rightarrow CH_3COOH + NH_4HSO_4,$$

or sodium salt:

$$CH_3CONH_2 + NaOH \rightarrow CH_3COONa + NH_3;$$

this reaction is accompanied by the formation of ammonia, which can easily be recognized by its odor.

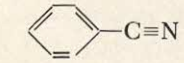
Amides treated with a dehydrating agent (phosphoric anhydride) are transformed into nitriles ($-C\equiv N$):

$$CH_3CONH_2 \xrightarrow[-H_2O]{P_2O_5} CH_3C\equiv N.$$

Nitriles can be considered derivatives of hydrocyanic acid (prussic acid) and are obtained by substituting the hydrogen atom with an organic radical:

$CH_3\equiv N$ methyl cyanide (acetonitrile)

$CH_3CH_2C\equiv N$ ethyl cyanide (propionitrile)



benzonitrile

Halides also can be heated with an alkaline cyanide in a solvent that dissolves both the reagents to form nitriles:

$$CH_3Cl + KCN \rightarrow KCl + CH_3CN$$

Nitriles, like amides, are transformed into the corresponding acids by hydrolysis (acid or base). The triple bond makes them particularly reactive; they can add water to yield amides, and hydrogen to yield amines:

$$CH_3CN + H_2O \rightarrow CH_3CONH_2$$
$$CH_3CN + 2H_2 \rightarrow CH_3CH_2NH_2,$$

making them important to organic ch[illegible]ists. Industrially, acrylonitrile ([illegible] CH−CN) polymerizes easily to produce synthetic fibers.

The lower members of the carboxylic acid family have a sharp or acrid odor; the acids from C_4 through C_8 have a distinctly disagreeable smell. The odor of rancid butter and strong cheese is due to volatile carboxylic acids. The higher acids are practically odorless because of their low volatility.

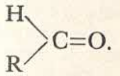
Many different acids of this family are widely distributed in nature. Citric acid, which makes up about 6 percent of the juice of an unripe lemon, is also found in many animal tissues, bone, and blood. Citiric acid is used as a medicine and in the manufacture of foods and beverages. Caproic acid is the source of the characteristic odor of goats. Formic acid is found in stinging nettles, in the bodies of ants and in some caterpillars.

Vinegar, a dilute solution of acetic acid, has been known since ancient times. Its principal use is in foods as a flavoring and preservative, but throughout history it has [illegible] regarded as having medicinal [illegible] Hippocrates prescribed it for his [illegible]ts. It was used with considerable success in treating scurvy during the Civil War. The manufacture of vinegar is a two-stage process involving the conversion of sugars to alcohol by yeasts and the conversion of alcohol to acetic acid by bacteria.

ALDEHYDES | preparation and properties

The functional group that identifies aldehydes and ketones is the carbonyl radical $>C=O$. The double bond between the carbon atom and the oxygen atom has such a high reactivity that carbonyl compounds can be considered a pillar of synthetic organic chemistry.

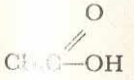
In aldehydes the carbonyl group is bonded to a hydrocarbon chain (R) and to a hydrogen atom:



$$\begin{matrix} H \\ R \end{matrix}\!\!>C=O.$$

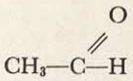
R can be an aliphatic, aromatic, alicyclic, or heterocyclic group. In the first member of the series, formaldehyde, R is a hydrogen atom.

The term *aldehyde* is derived from *alcohol dehydrogenatum* because aldehydes can be produced by removing hydrogen from primary alcohols. The different members of the series are distinguished by the name used for the corresponding acid:



$$CH_3—\overset{O}{\overset{\|}{C}}—OH$$

acetic acid



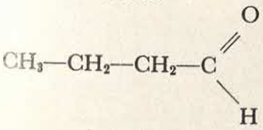
$$CH_3—\overset{O}{\overset{\|}{C}}—H$$

acetaldehyde

Reference can also be made to the name of the corresponding hydrocarbon; the name of the aldehyde is then obtained by adding the suffix *-al:*

$CH_3—CH_2—CH_2—CH_3$

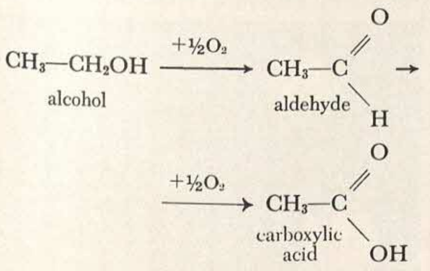
butane



$$CH_3—CH_2—CH_2—C\begin{matrix} \nearrow O \\ \searrow H \end{matrix}$$

butanal

With regard to degree of oxidation, aldehydes lie between the alcohols and the carboxylic acids:



$$\underset{\text{alcohol}}{CH_3—CH_2OH} \xrightarrow{+\frac{1}{2}O_2} \underset{\text{aldehyde}}{CH_3—C\begin{matrix} \nearrow O \\ \searrow H \end{matrix}} \rightarrow$$

$$\xrightarrow{+\frac{1}{2}O_2} \underset{\text{carboxylic acid}}{CH_3—C\begin{matrix} \nearrow O \\ \searrow OH \end{matrix}}$$

PROPERTIES

The group CHO which is to be found in all aldehydes contains the most active form of the carbonyl function known to chemists, and it is to the intense reactivity of this function that the aldehydes owe their importance as organic synthetic agents both in nature and in the chemical laboratory. Many aldehydes are known; some are produced artificially, while others are found in plants.

The aliphatic aldehydes contain members that are gases (formaldehyde and acetaldehyde), liquids (from 3 to 11 carbon atoms), and solids (12 or more carbon atoms) at ordinary temperatures.

Lower molecular weight aldehydes have penetrating and generally unpleasant odors. The odor changes gradually, however, as molecular weight increases. It eventually becomes pleasant in the 8 to 14 carbon atom group. Some of these compounds are actually used in perfumery.

Some aldehydes are produced industrially as intermediate compounds in organic syntheses.

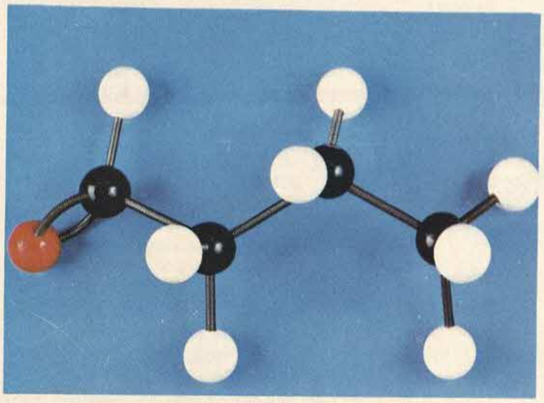
Other uses of aldehydes, apart from those connected with the production of perfumes, will be examined later.

PREPARATION

The raw materials for the preparation of aldehydes are principally alcohols, carboxylic acids, and unsaturated hydrocarbons.

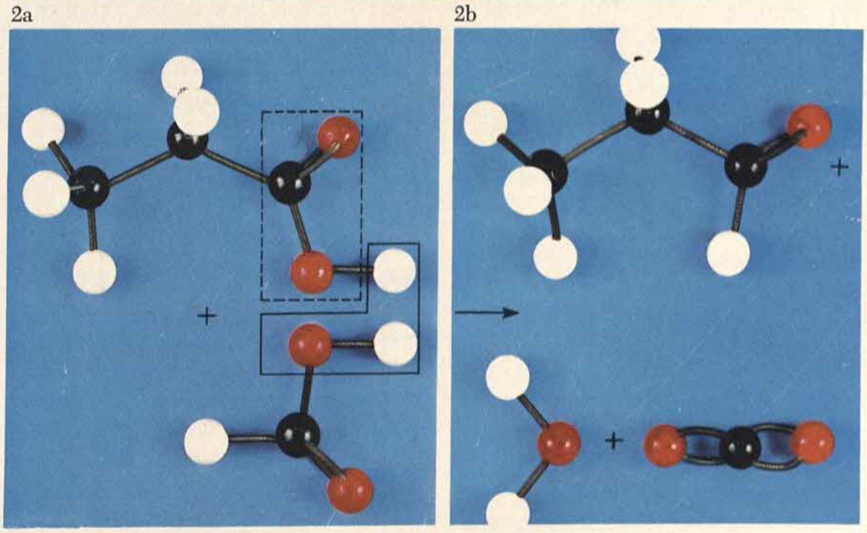
a. A method of fundamental importance for both industrial and laboratory preparation of aldehydes is oxidation

1



n-BUTYRALDEHYDE — This aldehyde—chemical formula $CH_3CH_2CH_2CHO$ — is also known as butanal, the name being derived from the corresponding hydrocarbon.

This compound is a liquid at ordinary temperatures (it freezes at −99° C or −146.2° F and boils at 76° C or 168.8° F). It is quite soluble in water (7 g of the aldehyde dissolve in 100 g of water).

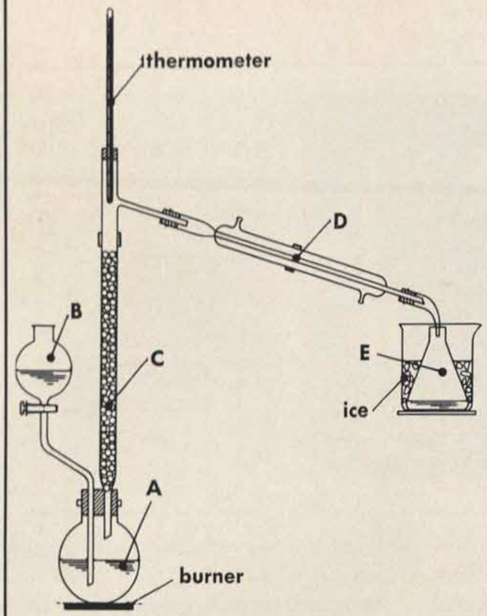


2a

2b

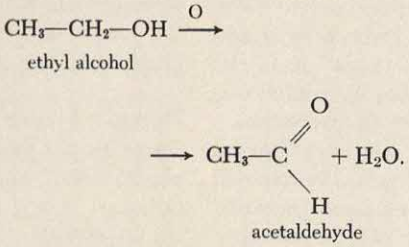
PREPARATION OF PROPIONALDEHYDE—An important preparation widely used in laboratory syntheses consists of converting carboxylic acids into aldehydes. The acid is reduced by passing its vapors (together with formic acid) over titanium oxide at high temperatures. In the case of propionaldehyde the starting material is propionic acid. The reaction with formic acid (Illustration 2a) takes place at 300 to 330° C (572 to 626° F). The aldehyde is produced along with carbon dioxide and water (Illustration 2b). Propionaldehyde is a liquid at ordinary temperatures. It freezes at −81° C (−113.8° F) and boils at 49° C (120.2° F).

3



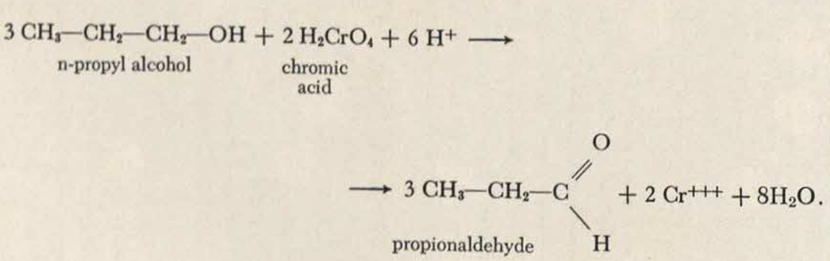
PREPARATION OF ALDEHYDES WITH LOW FREEZING POINTS—Flask **A** in the diagram contains n-propyl alcohol, while the dropping funnel **B** contains an aqueous solution of sodium bichromate and sulfuric acid. Flask **A** is heated; the oxidizing agent is then added as soon as the alcohol shows signs of boiling, the rate of dropping being adjusted to limit the temperature rise caused by the exothermic character of the reaction. The aldehyde, a more volatile substance than the corresponding alcohol, distills off very rapidly. The rectification column **C** ensures a better separation of the alcohol and the aldehyde. The cold water circulated through the water jacket **D** then serves to condense the aldehyde vapors. Liquid aldehyde is collected in the flask **E**, which is immersed in ice.

of primary alcohols:



$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} \xrightarrow{O} \underset{\text{acetaldehyde}}{CH_3-C\overset{O}{\underset{H}{\lessgtr}}} + H_2O.$$

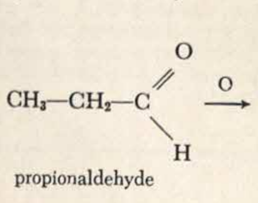
In industrial processes this reaction is carried out in the gas phase with air as the oxidizing agent. This process is treated in greater detail in another article. In the laboratory the oxidation is carried out in the liquid phase with chromic acid (obtained from sodium bichromate, $Na_2Cr_2O_7$) and sulfuric acid:

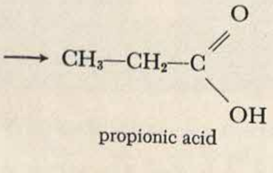


$$3\,\underset{\text{n-propyl alcohol}}{CH_3-CH_2-CH_2-OH} + 2\,\underset{\text{chromic acid}}{H_2CrO_4} + 6\,H^+ \longrightarrow 3\,\underset{\text{propionaldehyde}}{CH_3-CH_2-C\overset{O}{\underset{H}{\lessgtr}}} + 2\,Cr^{+++} + 8H_2O.$$

As indicated, the hexavalent chromium of chromic acid acts as the oxidizing agent and is reduced to the trivalent state.

These reactions must be controlled carefully to prevent further oxidation of the aldehyde to a carboxylic acid:

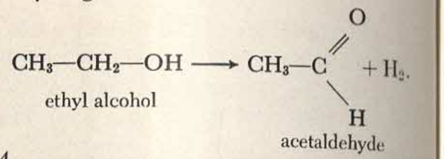




$$\underset{\text{propionaldehyde}}{CH_3-CH_2-C\overset{O}{\underset{H}{\lessgtr}}} \xrightarrow{O} \underset{\text{propionic acid}}{CH_3-CH_2-C\overset{O}{\underset{OH}{\lessgtr}}}$$

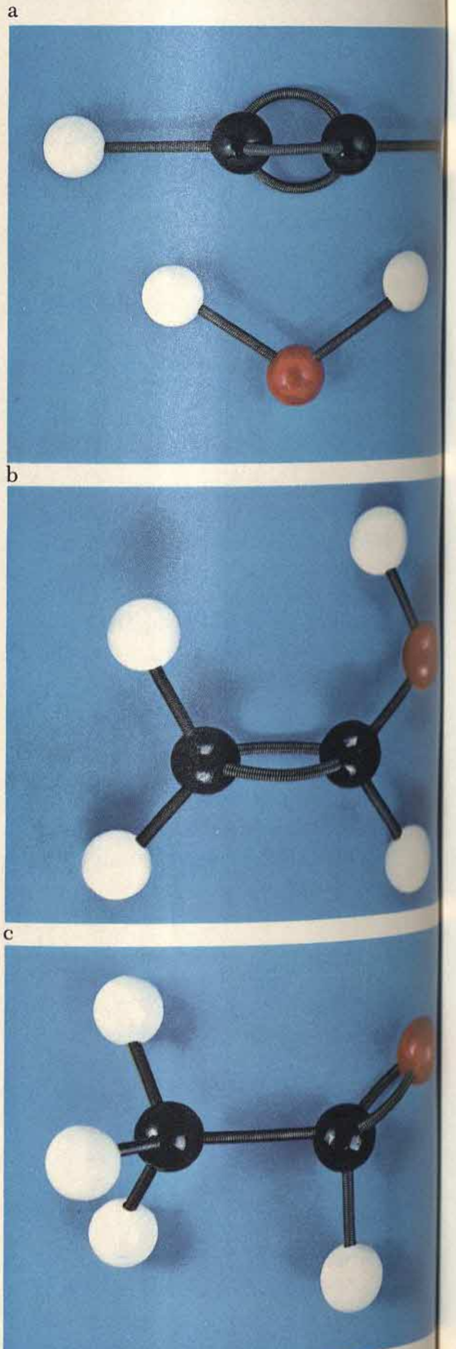
This subsequent oxidation can be avoided by immediately removing the aldehyde from the reagent mixture.

Conversion of a primary alcohol into an aldehyde can also occur in the absence of an oxidizing agent as a result of simple dehydrogenation:



$$\underset{\text{ethyl alcohol}}{CH_3-CH_2-OH} \longrightarrow \underset{\text{acetaldehyde}}{CH_3-C\overset{O}{\underset{H}{\lessgtr}}} + H_2.$$

4

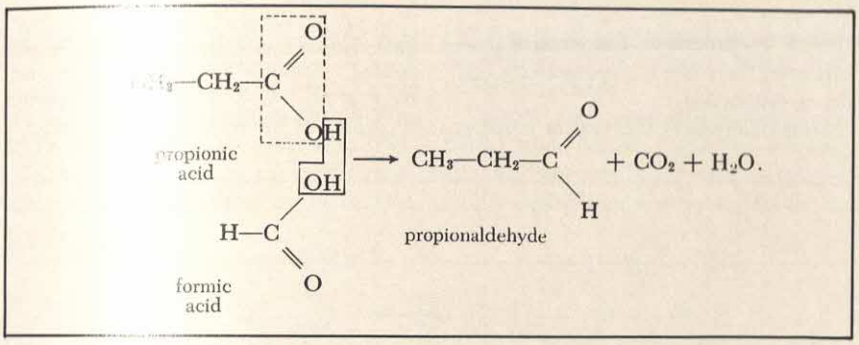


PREPARATION OF ACETALDEHYDE—The conversion of acetylene into acetaldehyde is an important industrial process. The hydration of acetylene (Illustration 4a) is carried out in the presence of sulfuric acid and mercuric sulfate. This leads to the unstable product vinyl alcohol (Illustration 4b), which immediately isomerizes into acetaldehyde (Illustration 4c). Acetaldehyde freezes at −121° C (−185.8° F) and boils at 20° C (68° F). It is highly soluble in water.

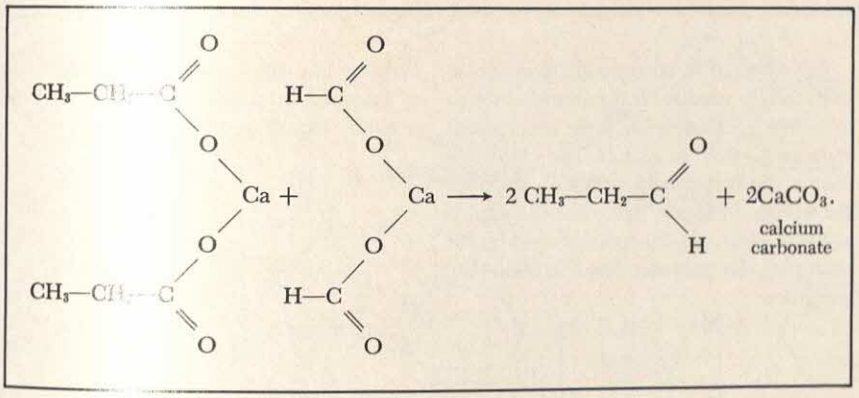
This reaction calls for temperatures of the order of 300° C (572° F) and copper-based catalysts.

b. The conversion of carboxylic acids into aldehydes is of primary interest for laboratory preparations and can be carried out in various ways.

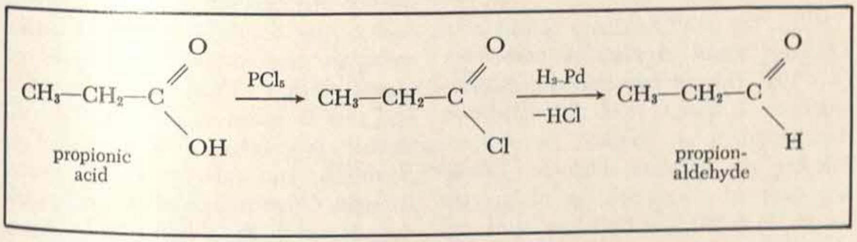
The carboxylic acid can be reduced by passing its vapors over titanium oxide at 300 to 330° C (572 to 626° F) together with formic acid:



An analogous reaction is produced by heating a mixture of the corresponding calcium salts (calcium propionate and calcium formate):



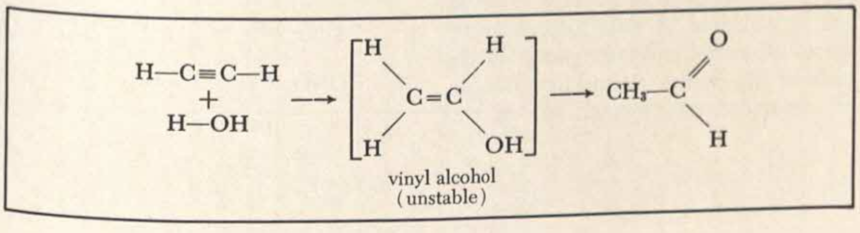
Chlorides of the acids, which can be obtained from carboxylic acids by treatment with chlorinating agents—phosphorus(V) chloride, for example—are readily reduced to aldehydes by hydrogen in the presence of a palladium catalyst (Rosenmund reaction):



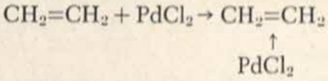
This reaction may be made to occur in the liquid phase by bubbling hydrogen through a hot solution of the chloride in xylene and maintaining the catalyst in suspension.

c. The conversion of unsaturated hydrocarbons into aldehydes is of considerable industrial interest, particularly in view of the low cost of starting materials such as acetylene, ethylene, propylene, and isobutylene.

The hydration of acetylene to form acetaldehyde occurs in the presence of sulfuric acid and mercury sulfate (the catalyst). The initial product of the addition of water is vinyl alcohol, an unstable compound that immediately isomerizes into acetaldehyde:

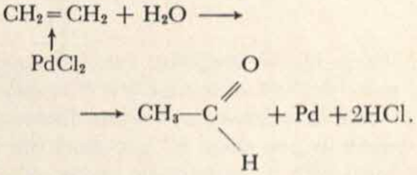


The conversion of ethylene into acetaldehyde makes use of molecular oxygen in dilute aqueous solutions of hydrochloric acid containing palladium and copper(II) chloride. This reaction takes place at moderate temperatures and pressures. It is now the basis of important industrial processes. The mechanism of this interesting oxidation includes the formation of a complex compound of ethylene and palladium chloride:



$$CH_2{=}CH_2 + PdCl_2 \rightarrow \underset{\overset{\uparrow}{PdCl_2}}{CH_2{=}CH_2}$$

Hydrolysis of this complex, accompanied by oxidation of the ethylene to aldehyde and reduction of the salt to a metal, follows:



The palladium chloride is regenerated as a result of oxidation of palladium metal by the copper(II) chloride

$$\underset{\text{copper(II) chloride}}{2\,CuCl_2} + Pd \rightarrow \underset{\text{copper(I) chloride}}{2\,CuCl} + PdCl_2.$$

Finally, the copper(II) chloride is regenerated by oxidation of the copper(I) chloride by oxygen:

$$2\,CuCl + 2\,HCl + \tfrac{1}{2}\,O_2 \rightarrow 2\,CuCl_2 + H_2O.$$

Thus, oxygen plays only an indirect part in the oxidation of the ethylene. Conversion of the ethylene is ensured by catalytic quantities of the two chlorides, since the copper(II) chloride is continually regenerated by the oxygen. The copper(II) chloride then regenerates the palladium chloride.

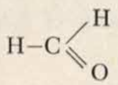
A reaction of unsaturated hydrocarbons of considerable industrial interest makes it possible to produce aldehyde molecules that have one more carbon atom than the hydrocarbon used in the preparation. This reaction is carried out at temperatures between 100 and 200° C (212 and 392° F) and at a pressure of 200 atmospheres (about 2,940 lb/sq in.). Cobalt tetracarbonyl, $Co_2(CO)_8$, acts as a catalyst.

The characteristic reactions of aldehydes and methods of preparation of aromatic aldehydes will be discussed in greater detail in other articles.

FORMALDEHYDE | preparation and industrial applications

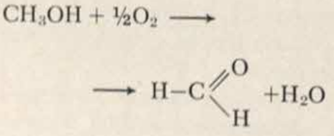
The importance of aldehydes as intermediates in the preparation of organic and polymeric materials is best appreciated by examining those members of the series that are of particular industrial interest. This article is thus devoted to formaldehyde.

Formaldehyde has the chemical formula:

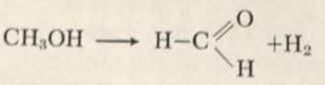


It is a highly irritating, colorless gas formed during the incomplete combustion of organic substances. Because formaldehyde is poisonous, all personnel concerned with its preparation or the production of its derivatives must submit to periodic medical examinations. Formaldehyde is obtained in large quantities by means of the oxidation of methyl alcohol and also by partial oxidation of the higher molecular weight hydrocarbons.

Production of formaldehyde from methyl alcohol is accomplished by passing the vapors of the alcohol (together with air) over copper or silver at temperatures of the order of 450 to 650° C (842 to 1,202° F) or over iron and molybdenum oxide catalysts at 300 to 400° C (572 to 752° F). In the first case oxidation and dehydrogenation take place simultaneously:



$$\mathrm{CH_3OH} + \tfrac{1}{2}\mathrm{O_2} \longrightarrow \mathrm{H{-}C}\begin{matrix}{/\!\!/}\mathrm{O}\\ \diagdown\mathrm{H}\end{matrix} + \mathrm{H_2O} \qquad (1)$$

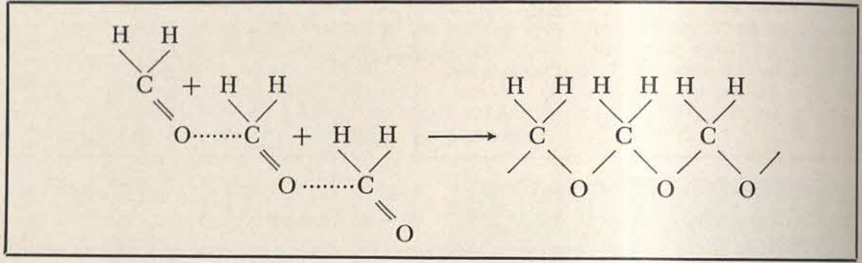


$$\mathrm{CH_3OH} \longrightarrow \mathrm{H{-}C}\begin{matrix}{/\!\!/}\mathrm{O}\\ \diagdown\mathrm{H}\end{matrix} + \mathrm{H_2} \qquad (2)$$

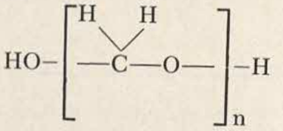
In the second case only oxidation occurs.

The production of formaldehyde from hydrocarbons is based on a partial oxidation carried out either with air or oxygen under pressure and at temperatures that depend on the starting materials. With butane, for example, the reaction is carried out at 400° C (752° F) and at 20 atmospheres. In addition to formaldehyde, a large number of secondary products, including acetaldehyde and methyl alcohol, are produced. The reaction products must therefore be separated by fractional distillation.

Formaldehyde is very easily polymerized because of the presence of the double carbon-oxygen bond (the carboxyl group $>C{=}O$). The reaction occurs according to the following mechanism:



Polymerization of formaldehyde occurs particularly readily in the liquid state or in solution. Moreover, it is accelerated by water, acids, or alkalis. The catalyst—that is, the water, acid, or alkali—supplies the groups of atoms that close the chains at their ends. In the case of water, for example, the polymer has the following structure:



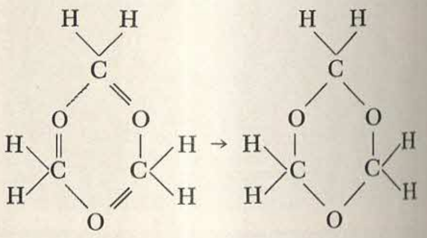
$$\mathrm{HO-}\left[\begin{matrix}\mathrm{H}\quad\mathrm{H}\\ \diagdown\diagup\\ \mathrm{-C-O-}\end{matrix}\right]_n\mathrm{-H}$$

In this polymer the hydrogen atom and the hydroxyl group are derived from a water molecule.

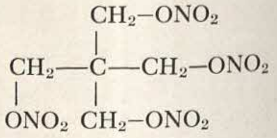
When the polymer chains consist of a relatively small number of monomers ($n < 100$), the polymer—called paraformaldehyde—is a white solid. This substance depolymerizes on heating, thereby reforming the original aldehyde. Linear polymers of formaldehyde of greater length ($n > 100$), on the other hand, are generically known as polyoxymethylenes. When n is a particularly large number, the products have plastic properties. In view of the low cost of formaldehyde, these substances are of great commercial importance.

A disadvantage of these polymers is their low thermal stability and their poor resistance to acids. A considerable improvement in their properties, however, can be obtained by stabilizing them by means of special molecular groups at the ends of the chains. Delrin, for example, is a modified polyoxymethylene of this type; it has good plastic properties.

Trioxane, a stable crystalline solid, is a cyclic trimer of formaldehyde:



A wide range of products is obtained from the reactions of formaldehyde with urea, melamine, and phenol. Urea resins are used in electrotechnology, in the production of recording disks, as adhesives, and in the textile industry. Melamine resins are used for producing laminated plastic products. Finally, phenolic resins find uses in terms of their excellent dielectric properties, their resistance to chemicals, and their great mechanical strength. Other industrial uses of formaldehyde are in the preparation of hexamethyltetramine and pentaerythritol, a tetravalent alcohol, $C(CH_2OH)_4$, easily prepared from acetaldehyde and formaldehyde. It is used to produce resins and also the explosive pentrite, prepared by complete esterification of the four alkoxy groups with nitric acid:



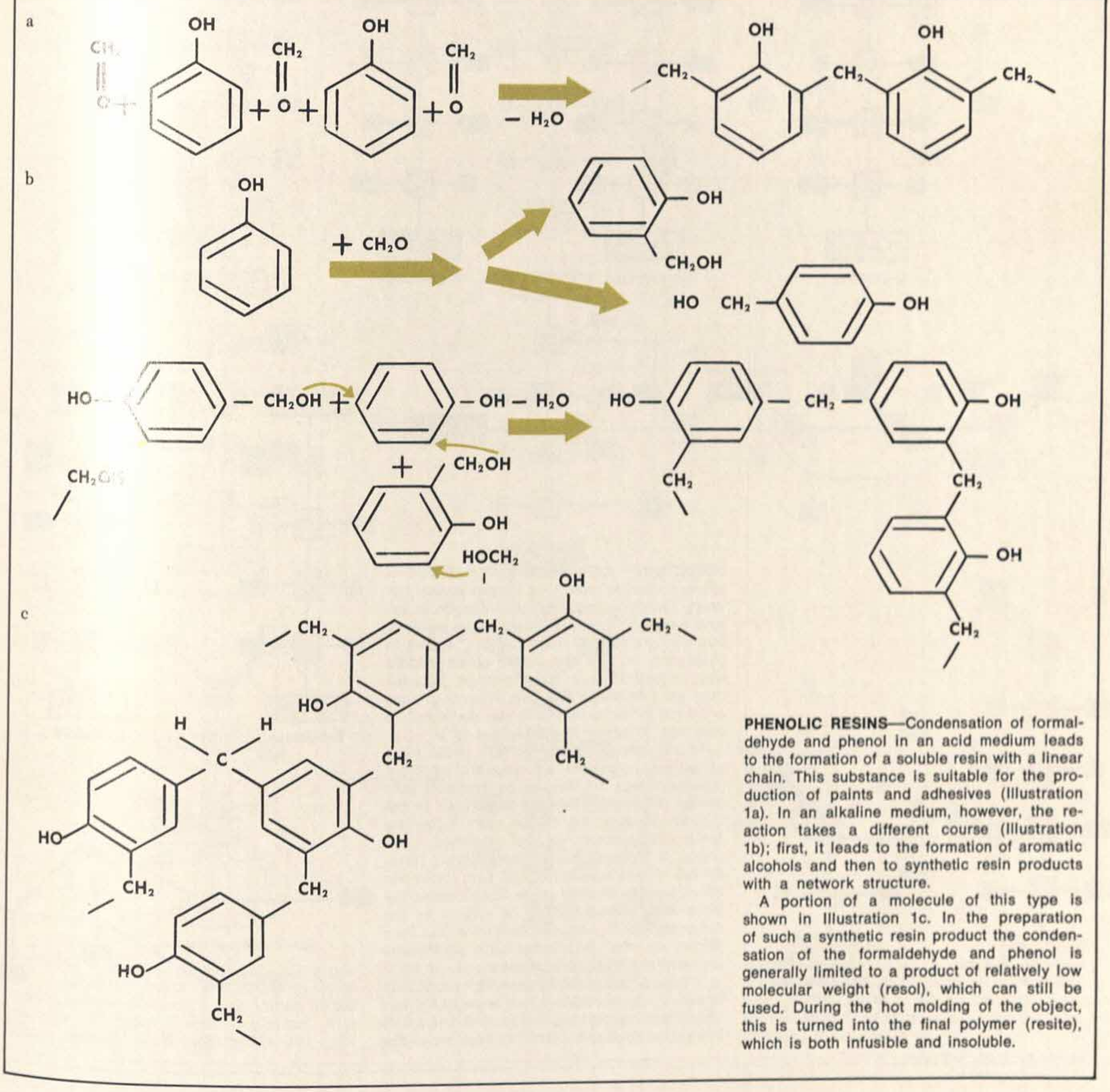
$$\begin{array}{lll} & \mathrm{CH_2{-}ONO_2} & \\ & | & \\ \mathrm{CH_2}{-\!\!-} & \mathrm{C}{-\!\!-}\mathrm{CH_2{-}ONO_2} & \\ | & | & \\ \mathrm{ONO_2} & \mathrm{CH_2{-}ONO_2} & \end{array}$$

pentrite

Pentrite, a pentaerythritol tetranitrate, is a sensitive high explosive. It is used also in medicine as a vasodilator. It was not in systematic use before World War II, although it was first prepared in 1891. Like most military high explosives, pentrite was used only after their detonation (by means of detonators) became well understood. It is usually mixed with other ingredients.

Various other synthetic products produced from formaldehyde find application in the textile and paper industries, in the pharmaceutical field, and in the rubber industry (accelerators and antioxidation agents). Finally, formaldehyde itself is used as a fungicide, deodorant, and disinfectant. For these purposes, it is supplied as formalin—an aqueous solution containing 37 to 50 percent formaldehyde by weight.

1



PHENOLIC RESINS—Condensation of formaldehyde and phenol in an acid medium leads to the formation of a soluble resin with a linear chain. This substance is suitable for the production of paints and adhesives (Illustration 1a). In an alkaline medium, however, the reaction takes a different course (Illustration 1b); first, it leads to the formation of aromatic alcohols and then to synthetic resin products with a network structure.

A portion of a molecule of this type is shown in Illustration 1c. In the preparation of such a synthetic resin product the condensation of the formaldehyde and phenol is generally limited to a product of relatively low molecular weight (resol), which can still be fused. During the hot molding of the object, this is turned into the final polymer (resite), which is both infusible and insoluble.

THE MONOSACCHARIDES

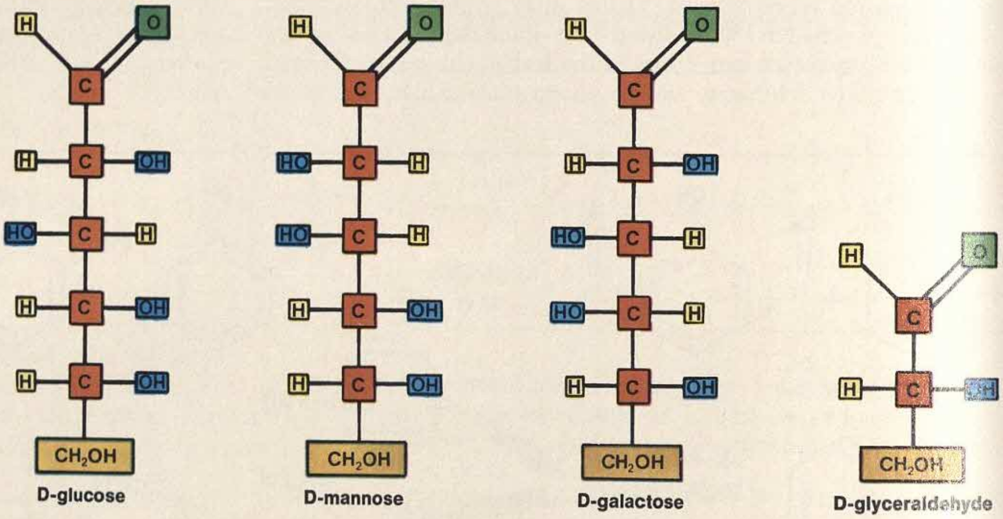
eight pairs of optical antipodes

A principal source of food for animals including man, the carbohydrates (sugars, starches, and celluloses) are vital to the life cycle. Most carbohydrates are formed by green plants in sunlight, through photosynthesis; this same process also restores oxygen to the atmosphere.

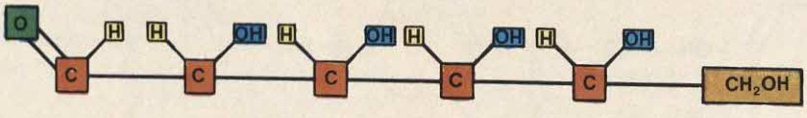
The term *carbohydrate* derives from the fact that the general formula of this class of substances may be represented by $C_x(H_2O)_y$, where the coefficients x and y can vary widely. Such a formula, being inexact, only reflects the quantitative relationships between the carbon, hydrogen, and oxygen atoms. The chem-

1

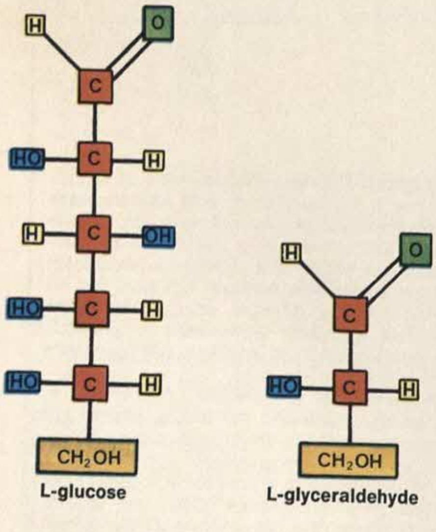
b


D-glucose D-mannose D-galactose D-glyceraldehyde

a



c

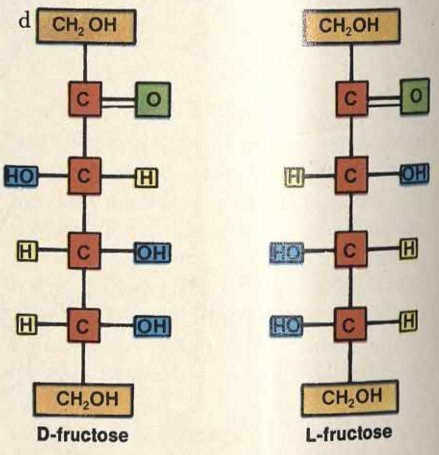

L-glucose L-glyceraldehyde

STRUCTURE OF MONOSACCHARIDES— Monosaccharide molecules contain several hydroxyl functions and either an aldehyde or ketone function. The best known of the series is that with six carbon atoms (hexose) shown in Illustration 1a. The four carbon atoms marked with an asterisk are dissymmetrical because they are substituted with four different groups, and exist in two antipodal forms; the molecule thus has 16 isomeric possibilities (2^4).

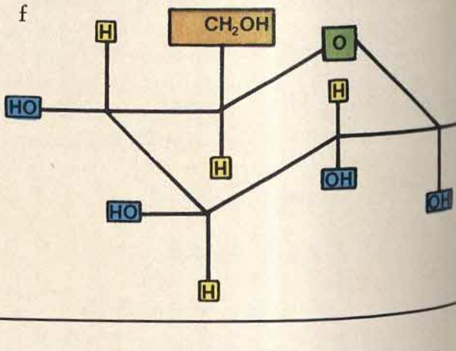
All 16 optically active isomers (eight pairs of optical antipodes) are known. The more important ones are derived by Fischer's projection (Illustration 1b) and are shown in the D-forms because the carbon atom 5 has the same configuration as the reference compound, D-glyceraldehyde. The L- forms (Illustration 1c) are analogous, and both forms are mirror images of each other. Each causes the plane of polarized light to be rotated by the same amount in opposite directions, but they display no other differences either in physical properties or chemical behavior.

Fructose, one of the ketones with six carbon atoms, is also a constituent of important disaccharides (Illustration 1d). The carbonyl group in fructose is usually combined with one of the

d


D-fructose L-fructose

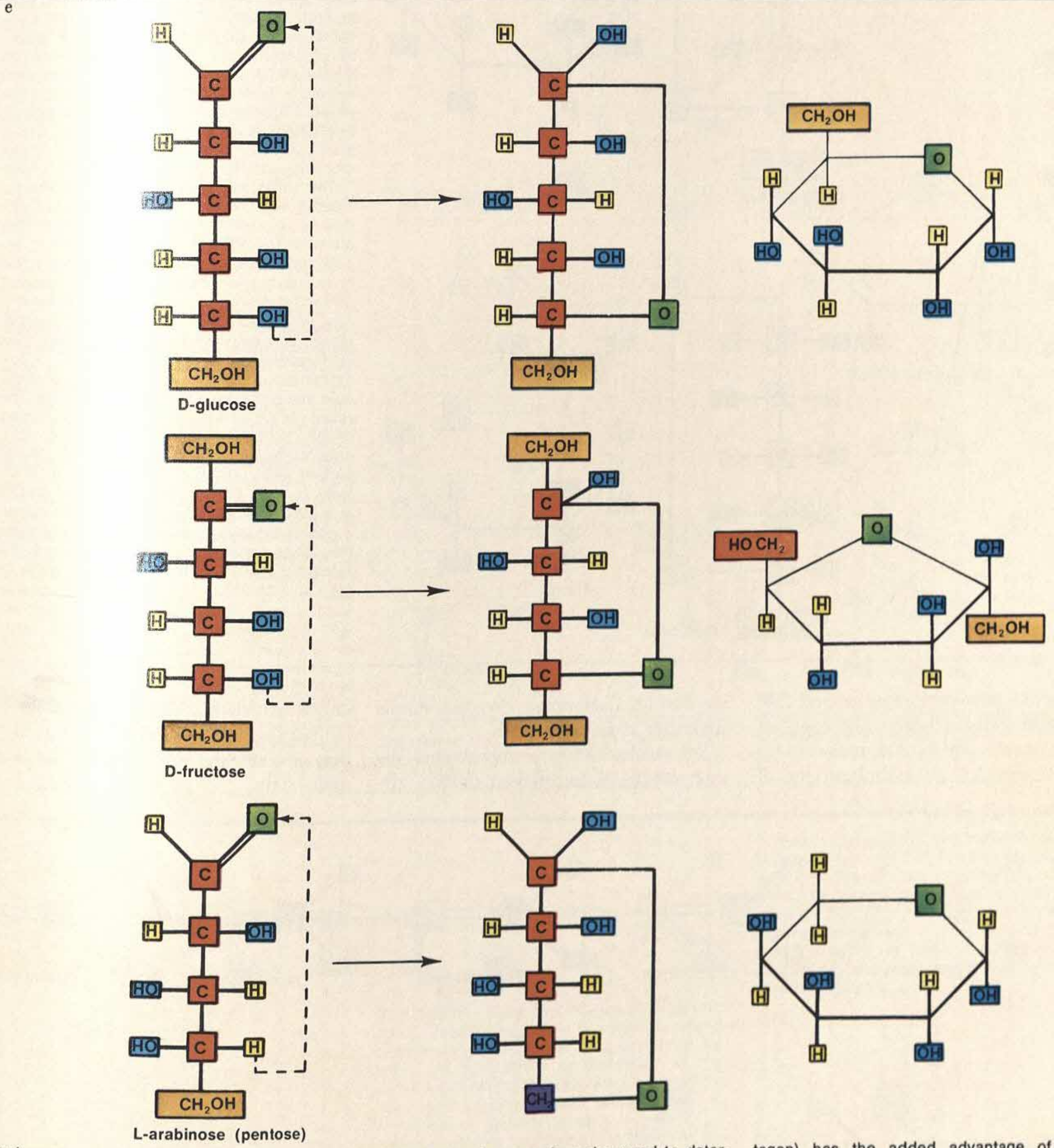
f



ical nature of carbohydrates is derived from the presence of both hydroxyl (alcohols) and carbonyl (ketones, aldehydes) groups.

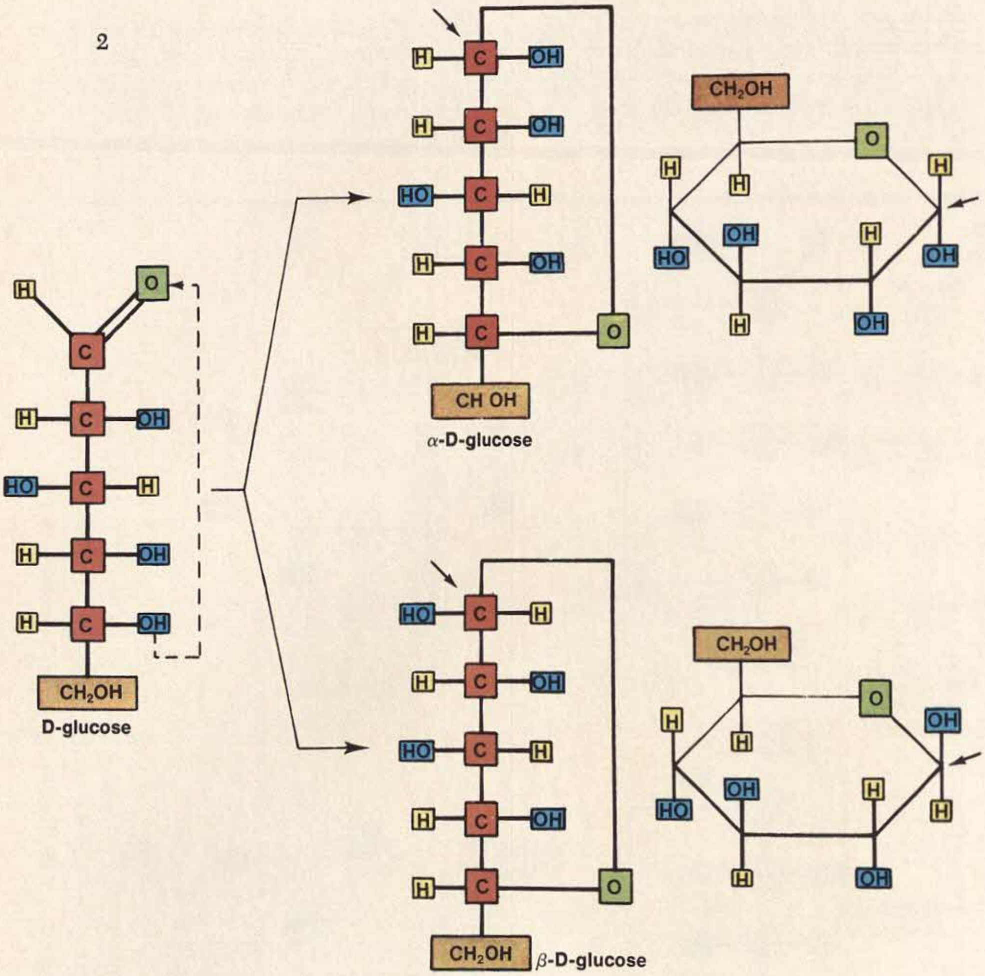
Three main subdivisions of carbohydrates are recognized—monosaccharides, disaccharides, and polysaccharides. All are characterized by quite different physical properties and chemical behavior.

Monosaccharides include the simple sugars fructose, glucose) and they are characterized by their generally sweet taste and their solubility in water. Many of the early experiments on mono-



hydroxyls in the molecule; the linkage is due to a semiacetal bond (Illustration 1e—note that a hydrogen molecule has shifted in the formation of these cyclic compounds). The cyclic structure better reflects the real state of the molecule; open formulas used to determine the configuration of various hexoses are thus abandoned. Two cyclic representations of D-glucose, D-fructose, and L-arabinose (pentose) are shown; the second (hexagon, or pentagon) has the added advantage of being closer to the real configuration of the molecule. In the case of crystalline D-glucose, x-ray studies have demonstrated the chairlike structure of Illustration 1f.

2



PROPERTIES OF MONOSACCHARIDES— Sugars dissolve easily in water, and to a lesser extent in ethyl or methyl alcohol; they are insoluble in ether and other organic solvents. A fundamental property of monosaccharides is their optical activity. In this connection, substances containing dissymmetrical carbon atoms do not display any rotation with respect to polarized light when synthesized in the laboratory. In fact, the D and L antipodes are formed in equal quantities (their chemical and physical properties are identical), and opposite rotations balance each other. Natural synthesis, however, leads to the formation of only one antipodal form.

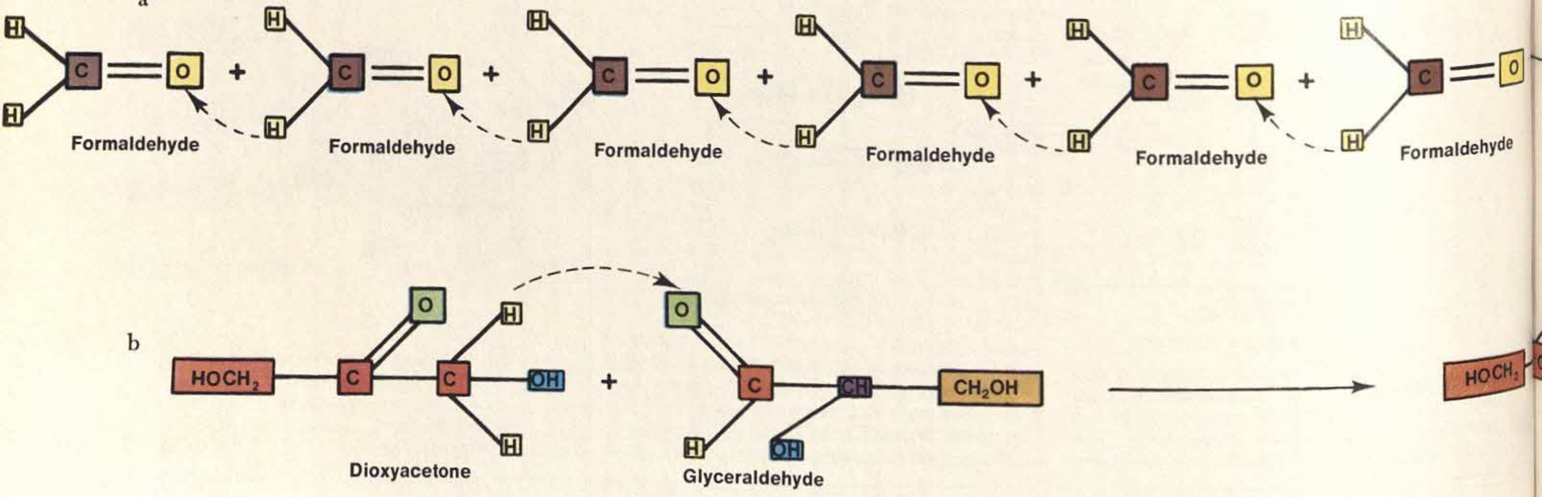
The rotational powers of the monosaccharides in aqueous solutions undergo a variation that is unusual among optically active substances. The specific rotational power of glucose, for example, amounts to $(\alpha)_D = +112°$ immediately after the substance has dissolved, and will decrease slowly to a constant value of $(\alpha)_D = +52.5°$. This phenomenon (mutarotation) is explained by the existence of the cyclo-semiacetal form, which creates a new asymmetrical carbon atom in the sugar molecule that can exist in two antipodal forms. This results in the formation of two different isomers of the cyclic molecule (α and β), which differ only according to the configuration of the first carbon atom (arrow). The specific optical activity is thus $(\alpha)_D = +112°$ for α-D-glucose and $(\beta)_D = +18.7°$ for β-D-glucose. In water, a part of the isomer will gradually transfer into the other until equilibrium is reached; the rotational power of this mixture is given by $(\alpha)_D = +52.5°$.

saccharides were performed around 1890.

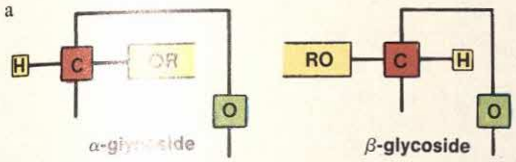
Disaccharides (lactose, maltose, sucrose) are formed by the union of two monosaccharides. In hydrolysis, the disaccharides decompose into the simple sugars, or monosaccharides.

Polysaccharides are represented by such substances as cellulose, dextrin, glycogen, and starch. These complex carbohydrates are either insoluble in water, or they are soluble only when in the colloidal state.

4



3



ORIGINS OF MONOSACCHARIDES—D-glucose and D-fructose are found in a free state in honey, fruit, and plants. Glycosides are an important natural source of sugars and under hydrolysis (enzyme, acid, or alkali) produce sugar and either alcohol or phenol. Glycosides take the name of the sugar involved; glucoside if glucose, galactoside if galactose, and so forth. The nonsugar component is bound to the semiacetal carbon atom of the sugar as shown in Illustration 3a.

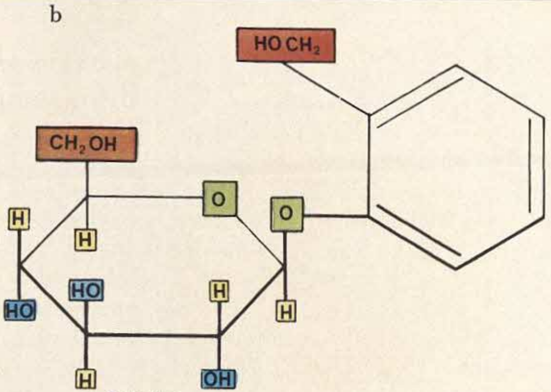
Alpha and beta glycosides depend on whether the sugar is the α or β isomer. In enzyme hydrolysis,

$$C_6H_{11}O_5-OR + H_2O \underset{\text{glucose}}{\overset{\text{enzyme}}{\rightleftarrows}} C_6H_{12}O_6 + ROH.$$

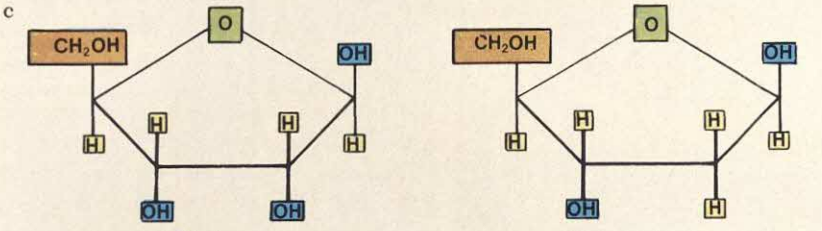
Enzyme activity is thus closely related to the glycoside configuration. Some enzymes (α-glycosidases) split only the alpha-glycosides, while others (β-glycosidases) react only on beta-glycosides.

The function of glycosides in plants is not clear, but it is known that some medicinal properties of roots are connected to glycosides as a result of pronounced physiological action. The formula of one of the β-glycosides (salycine, or willow bark) is shown in Illustration 3b. The nonsugar component in salycine is represented by o-hydroxyl-benzylic alcohol.

Aside from the O-glycosides (alcohols or phenols bound to the semiacetal carbon atom by an oxygen bridge), some N-glycosides are constituents of biologically active molecules. In these N-glycosides, the sugar (five carbon atoms) can be either D-ribose or 2-deoxy-D-ribose as shown in Illustration 3c. In the case of adenosine, the sugar is D-ribose (Illustration 3d). When adenosine is esterified with an anhydride of phosphoric acid and further phosphorylated, it becomes adenosine triphosphate (ATP), a substance vital to the muscular activity of animals. Some N-glycosides are also related to the compounds RNA (ribonucleic acid) and DNA (deoxyribonucleic acid), which are found in all living cells and are responsible for the basic functions of life itself (for example, hereditary characteristics).

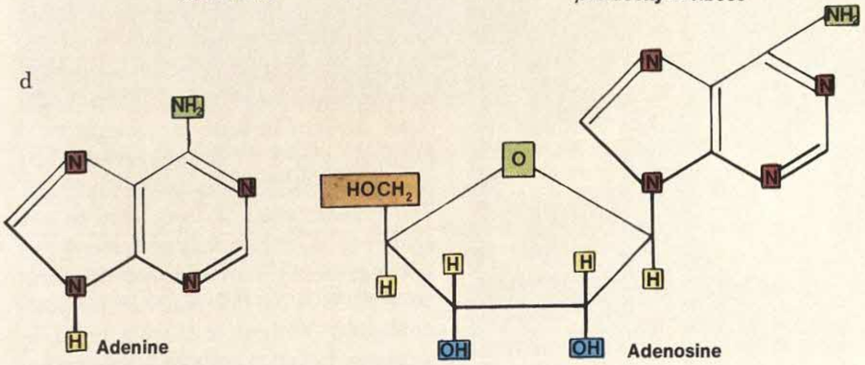


Salycine



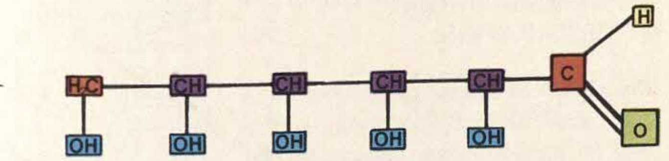
α-D-ribose

β-2-deoxy-D-ribose

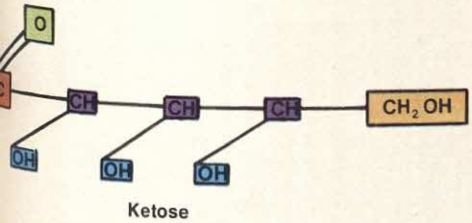


Adenine

Adenosine



Aldose



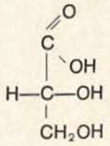
Ketose

SYNTHESIS—A complex mixture of sugars can be obtained by the action of alkalis on formaldehyde—a reaction that is represented formally, but not actually, by Illustration 4a. The same type of sugars can also be obtained from glyceraldehyde and dioxyacetone by condensation (Illustration 4b).

Carbohydrates are formed in green plants as the result of photosynthesis. This process consists of a reaction between the water and carbon dioxide absorbed by the plant:

$$yCO_2 + yH_2O \rightarrow \underset{\text{carbohydrate}}{(CH_2O)_y} + yO_2$$

Photosynthesis produces carbohydrates and oxygen; the oxygen is restored to the atmosphere in the process. Sunlight supplies the energy for the reaction, which is aided by the catalyst chlorophyll. The chlorophyll molecule is particularly reactive in sunlight and transmits this energy to other reactions. An intermediate product of photosynthesis is a derivative of D-glyceric acid:



$$\begin{array}{c} O \\ /\!\!/ \\ C \\ |\ \ \diagdown OH \\ H-C-OH \\ | \\ CH_2OH \end{array}$$

This product gives rise, through a series of reactions catalyzed by enzymes, to both simple sugars and more complex disaccharides and polysaccharides.

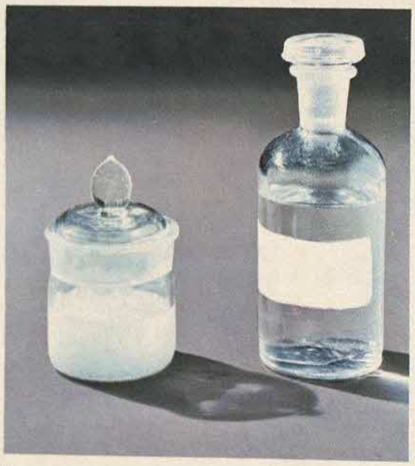
The most important source of monosaccharides is, of course, the disaccharides and polysaccharides themselves.

ACETIC ACID | a chemical produced by bacteria

Acetic acid, CH_3COOH, has been known since ancient times as the sour ingredient of vinegar. In fact, Pliny relates that Cleopatra occasionally sipped a drink produced by dissolving pearls in vinegar. Concentrated acetic acid, on the other hand, was first prepared about 200 years ago. Acetic acid is unusually abundant in the Plant Kingdom. Plants sometimes contain it in the free form, although for the most part it is combined with alcohols in the form of esters. It is also found in animal secretions. Many microorganisms and fermenting agents are capable of transforming organic substances into acetic acid. The compound is found in sour milk and in cheese. It is also formed during the fermentation of alcoholic liquids; this is how vinegar is produced from wine.

GLACIAL ACETIC ACID—Pure acetic acid is a colorless liquid. It crystallizes at 16° C (about 61° F) into crystals that are similar to those of ordinary ice. It irritates the skin and can also produce sores.

1



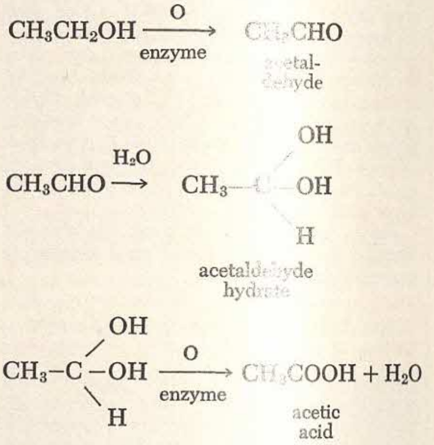
2

"MOTHER OF VINEGAR"—If *Mycoderma aceti* (more commonly known as "mother of vinegar") is placed in wine, acetic acid will be formed. This material contains the bacteria that cause fermentation of the alcohol in wine.

Pure acetic acid is a clear and colorless liquid with a pungent odor. In the anhydrous form it solidifies at 16° C (about 61° F) into crystals that are quite similar to ordinary ice crystals. This is the basis of the name glacial acetic acid. The acid is irritating to the skin and can produce painful sores. Aqueous solutions of the acid have a corrosive effect even on metals—aluminum, for example. This might cause concern because the vinegar used for cooking is a dilute solution of acetic acid, and so could attack kitchen utensils. The concentration of acetic acid in vinegar is so low (generally of the order of 5 to 6 percent), however, that the effect on utensils is for all practical purposes negligible. Vinegar is manufactured by a process in which carbohydrates are fermented to yield ethyl alcohol, which is then oxidized to acetic acid. Names such as malt vinegar or cider vinegar indicate the origins of the carbohydrates used in the fermentation process.

BIOLOGICAL METHODS OF PREPARATION

The ability of microorganisms to transform ethyl alcohol into acetic acid is used to produce wine vinegar for human consumption. Some acetic ferment ("mother of vinegar") is added to the wine and the liquid is allowed to stand undisturbed in a tepid place. After a time oxidation of the alcohol and formation of the acid takes place. This is called the Orléans process. The numerous bacteria of the *Acetobacter* type that make up the "mother of vinegar" contain an alcohol-oxidizing enzyme—a catalyst that uses the oxygen of the air to oxidize the ethyl alcohol, producing acetaldehyde as an intermediate product:



$$\underset{}{CH_3CH_2OH} \xrightarrow[\text{enzyme}]{O} \underset{\text{acetal-}\atop\text{dehyde}}{CH_3CHO}$$

$$CH_3CHO \xrightarrow{H_2O} \underset{\text{acetaldehyde}\atop\text{hydrate}}{CH_3-C(OH)(OH)H}$$

$$CH_3-C(OH)(H)-OH \xrightarrow[\text{enzyme}]{O} \underset{\text{acetic}\atop\text{acid}}{CH_3COOH} + H_2O$$

As these reactions show, the acetic bacteria oxidize the alcohol into an aldehyde. The hydrate of the aldehyde is then transformed into acetic acid by enzyme action.

The so-called fast process for producing acetic acid is more rapid than the Orléans process. In the fast process the oxidation of the alcohol is achieved by allowing it to drop into wood shavings.

Older factories for the production of acetic acid consisted of wooden vats filled with beech shavings (or some other cellulose material) which served as support for *Mycoderma aceti*, the microorganism that catalyzes the oxidation. The alcohol, obtained from the fermentation of molasses and separated by distillation, was then allowed to drop onto this material. The alcohol solution was diluted (12 to 15 percent in order to avoid killing the bacteria) and contained phosphate and ammonium salt additives that served as food for the microorganisms. The air needed for the oxidation was introduced from the bottom of the vat. The air was warmed by the heat emitted during the reaction, passed through the entire reacting mass, and then escaped from the top of the vat. The operation was carried out at a temperature of about 35° C (95° F). The product of this method was acetic acid having a concentration of about 10 percent.

The activity of the microorganism is

at its peak when the acid is in dilute concentrations. Moreover, it ceases altogether when the acid concentration exceeds 12 percent. These vats produced about 30 liters of dilute acid per day. The dimensions of the vats, which were about 1 m (about 3 ft) in diameter and 2.5 to 3 m (about 8 to 10 ft) high, could not be increased because of the difficulty of controlling the bacteria cultures. Modern plants, however, have been greatly improved and permit the use of much larger vats. A fermentation plant now operating in the United States, for example, is capable of producing 4,500 tons of acetic acid per year.

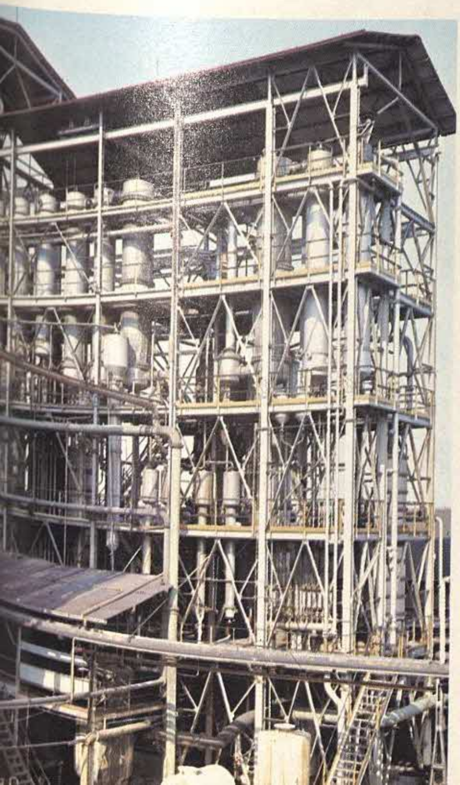
Wooden vats have now been replaced by ceramic towers filled with beech shavings and fitted with automatic spraying equipment at the top for feeding the alcohol into the tower. The alcohol, of course, must be adequately diluted.

DISTILLATION OF WOOD

Pyroligneous acid, a product obtained from the destructive distillation of wood, contains about 5 to 6 percent acetic acid in addition to methyl alcohol, oils, and various other compounds. In order to separate the acid from these other products, the mixture is first neutralized with lime:

$$\underset{\text{acetic acid}}{2\,CH_3COOH} + \underset{\text{lime}}{CaO} \rightarrow \underset{\text{calcium acetate}}{(CH_3COO)_2Ca} + H_2O.$$

PRODUCTION OF INTERMEDIATE ACETYLENE—This plant produces acetylene, which is then converted into acetic acid. The acetylene is produced by treating methane with water in the presence of mercury (II) sulfate, $HgSO_4$. The $HgSO_4$ acts as a catalyst.
3



4
PRODUCTION OF ACETIC ACID — Acetylene is first washed thoroughly with water, then passed through rectification columns, and finally oxidized in the presence of a suitable catalyst. The acetylene is oxidized into acetic acid in the apparatus illustrated.

The crude calcium acetate (calcium pyrolignite) is then treated with sulfuric acid to obtain calcium sulfate and acetic acid:

$$(CH_3COO)_2Ca + H_2SO_4 \rightarrow 2\,CH_3COOH + CaSO_4.$$

This acid is purified in part by treating it with an oxidizing agent (permanganate or bichromate) that eliminates impurities. Finally, distillation produces 99.5 percent pure acetic acid.

CHEMICAL SYNTHESES

The bulk of the acetic acid in use today is produced by the oxidation of acetaldehyde, which is obtained either from ethyl alcohol or from acetylene by means of hydration:

$$\underset{\text{acetylene}}{HC \equiv CH} + H_2O \xrightarrow[\text{mercury salts}]{H_2SO_4} \underset{\text{acetaldehyde}}{CH_3CHO}.$$

This method of synthesis is becoming increasingly more important. Indeed, acetic acid produced from acetylene is now about as plentiful as acetic acid produced from wood.

The oxygen of the air is the most economic oxidizing agent available; it is possibly also the most difficult to use. Although atmospheric oxygen always reacts with organic substances at ordinary temperatures, the reaction speed is generally too low under these conditions and does not produce an acceptable yield.

If molecular oxygen is to react at speeds suitable for industrial processes, a higher temperature as well as a catalyst must be used. Oxidation of acetaldehyde is made to occur in the presence of the catalysts, manganese acetate or cobalt acetate. The reaction temperature is of the order of 60° C (140° F) and the pressure is generally about 5 atmospheres. The reaction is complete in 12 to 14 hours. Traces of residual aldehyde are recovered by washing the exhaust gases; they are then put back into the cycle. This method produces acetic acid having a concentration of more than 96 percent.

If an arrangement is set up that removes acetic acid as it is formed and supplies new acetaldehyde as it is needed, the result yields acetic acid in concentrations of up to 90 percent.

Finally, acetic acid can be produced by the oxidation of ethane in the presence of a metallic catalyst:

$$CH_3CH_3 \xrightarrow[\text{100 atmospheres}]{\text{O, Cu}} CH_3COOH + CH_3CHO.$$

If a high yield of product is desired, a limited quantity of oxygen must be supplied. In addition, the hydrocarbon must be recycled.

USES OF ACETIC ACID

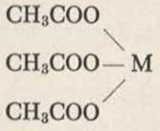
Acetic acid is of considerable industrial importance. In addition to its extensive use in vinegars, it is widely used as a solvent for resins and oil essences. It is also used in the synthesis of some perfumes and dyes. Acetone, an important industrial chemical, is produced by bringing the vapors of acetic acid into contact with scorching barium carbonate ($BaCO_3$) or pumice stone:

$$2\,CH_3COOH \xrightarrow{BaCO_3} CH_3COCH_3 + H_2O + CO_2$$

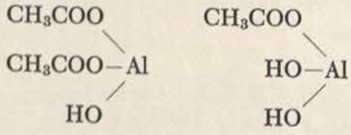
or by the decomposition of calcium acetate (calcium pyrolignite):

$$(CH_3COO)_2Ca \rightarrow CH_3COCH_3 + CaCO_3.$$

The commercial importance of acetic acid, however, lies primarily in its use as an acetylation agent of cellulose (together with acetaldehyde). Acetates of cellulose are used to prepare plastic substances similar to celluloid (cellite, cellon, acetate paints, plastic materials), for the production of film, and for the production of artificial silk (acetate silk). Acetylcelluloses are far less flammable than nitrocelluloses. They can, therefore, be used more frequently because no special precautions are required. The use of acetic acid in dyeing and fabric printing depends on the specific properties of some of its salts. The acetates of trivalent metals, which can be represented by the formula



(where M represents iron, aluminum, or chromium), are soluble in water. When hydrolyzed at high temperatures, however, they are converted into insoluble basic salts:



The formation of these salts is of great importance in the mordanting of textile fibers. This operation, which is preliminary to dyeing, fixes the dye firmly to the fiber. The cloth to be mordanted is wetted with a solution of aluminum or chromium acetate, allowed to dry, and then treated with steam. This converts the acetates into insoluble basic salts or into hydroxides. These remain mechanically fixed to the fibers. Together with appropriate dyes, they then give rise to insoluble colored substances. Colors produced by mordanting can generally be distinguished by their brilliant tones.

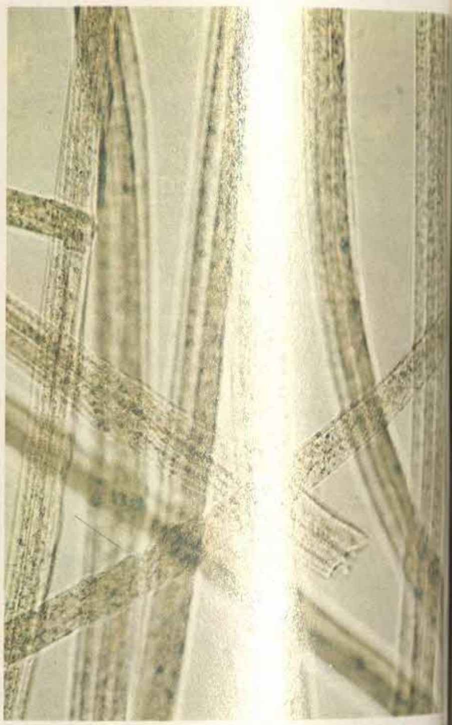
Lead acetates are used in the production of paints. Neutral lead acetate, often

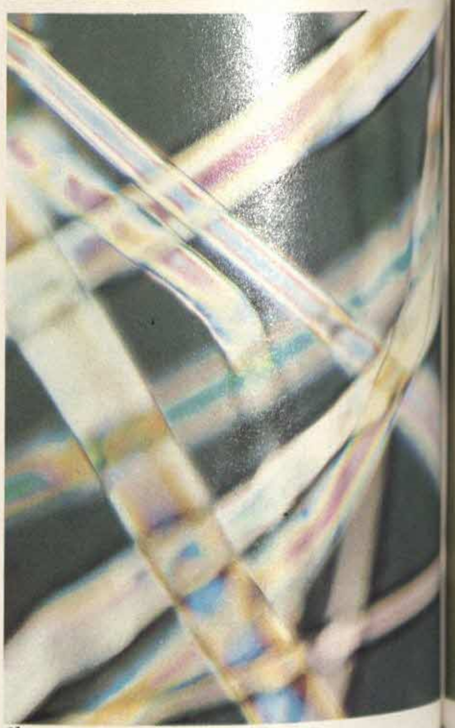
CELLULOSE ACETATE—Acetic acid is used as an acetylating agent of cellulose. The cellulose acetates thus produced are used to manufacture plastics similar to celluloid and artificial silk. Cellulose acetate thread is shown here.

5

ESTERS OF ACETIC ACID—This series of photomicrographs (250 X) shows a number of

6a





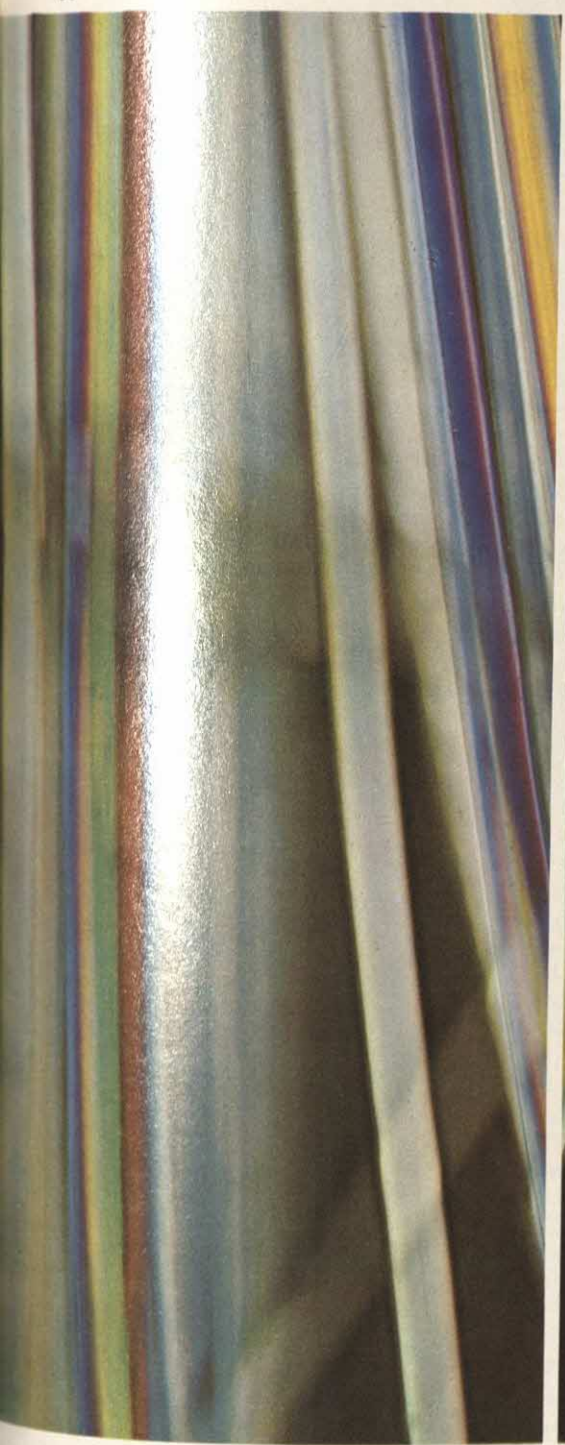
6b

called lead sugar because of its sweet taste, is used in white lead and chrome yellow. Acetates are used in medicine also. Aluminum acetate is a good antiseptic and astringent, while basic lead acetate is used for the treatment of bruises and also for burns.

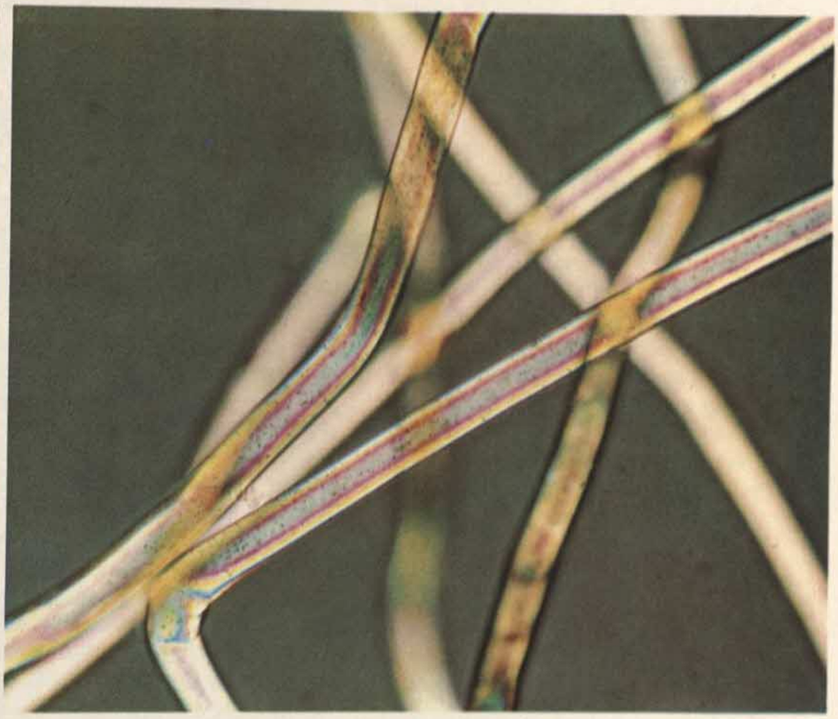
Acetic acid is also used in hydrogenation as a solvent with platinum and palladium-type catalysts only. It has been found desirable to conduct a hydrogenation in the presence of a suitable solvent particularly in the case of high-melting solids and compounds that react vigorously with hydrogen.

fibers produced by esterification of acetic acid. Illustration 6a shows fibers of rayon acetate, while Illustration 6b shows perlon fibers under polarized light. Illustration 6c, 6d, and 6e, all taken under polarized light, show other types of synthetic fibers.

6c



6d

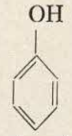


6e

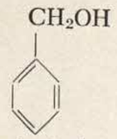
PHENOLS | dyes, medicines, plastics and perfumes from coal tar

Phenol, C_6H_5OH, one of the most important compounds used in the chemical industry, was first isolated from coal tar in 1834. Phenol is known also as carbolic acid because of its acid properties, which distinguish it from alcohols. A powerful disinfectant, phenol was used by Joseph Lister in the first antiseptic surgery, performed in 1865. In 1841 phenol was isolated in crystalline form and its composition was analyzed. It was then termed "phenylic acid," later shortened to phenol. In 1867 phenol was synthesized, and by the mid-twentieth century about 90 percent of its production was by synthesis.

The term "phenol" is used today to describe any hydroxylated compound in which at least one –OH (hydroxyl) group is directly attached to an aromatic group. If the hydroxyl appears in a side chain, the term "aromatic alcohol" (benzyl alcohol) is used:



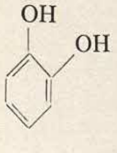
phenol



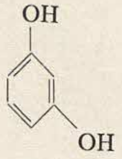
benzyl alcohol

Thus the term "phenol" is used to denote a whole family of compounds.

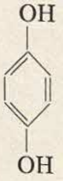
Examination of its structural formula reveals that phenol has no chance of exhibiting isomerism because all the positions of the ring are equivalent. When two hydroxyls are attached to the ring, three possibilities of isomers exist, depending on whether the second –OH group is in the ortho, meta, or para position:



catechol

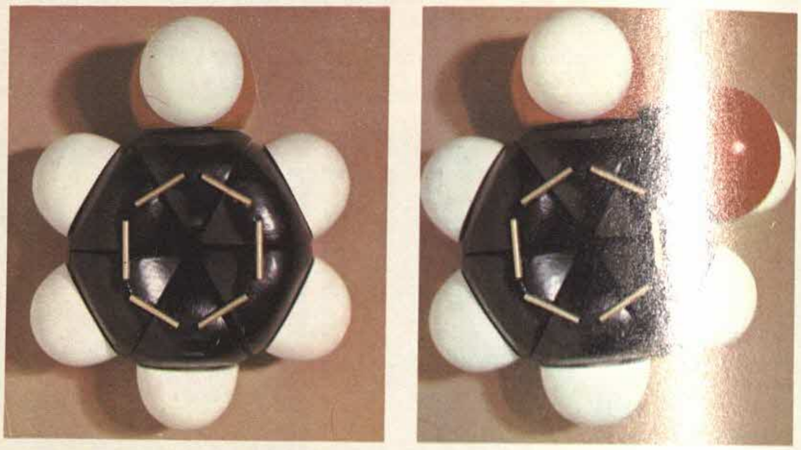


resorcinol



hydroquinone

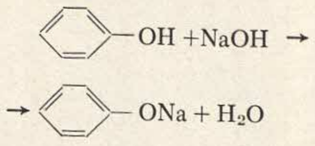
There are three triple-substituted derivatives (pyrogallol, phloroglucinol, and hydroxyhydroquinone), three tetrahydroxybenzenes, one pentahydroxybenzene, and finally one hexahydroxybenzene, in which all the hydrogens in the ring have been replaced by the same number of –OH.



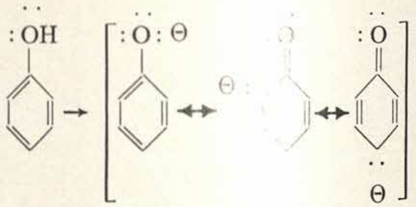
PHENOL AND CATECHOL—Phenol (Illustration 1a) was originally called phenylic acid because of the acid properties that distinguish it from alcohols; the name was later changed to phenol. Illustration 1b shows the structure of catechol.

PROPERTIES

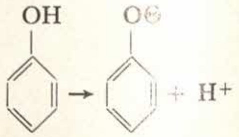
Phenol is more acid than are alcohols, and this property differentiates it from them. The aromatic radical increases the acidity of the hydroxyl. In the case of alcohols, substitution of the hydrogen by metals such as sodium only happens through the agency of the metal itself, as in the reaction $CH_3OH + Na \rightarrow CH_3ONa + 1/2H_2$, while the reaction $CH_3OH + NaOH \rightleftarrows CH_3ONa + H_2O$ is impossible, since the equilibrium is further to the left than to the right, as the length of the arrow shows. This means that water is a stronger acid than methyl alcohol and can thus detach it from its salts. In the case of phenol, on the other hand, the equilibrium of the reaction is well over to the right, confirming that phenol is a stronger acid than water, since the latter cannot detach the former from its salts.



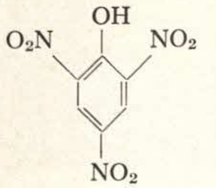
Phenol's superiority over alcohols in the matter of acidity is probably caused by resonance effect. The nondissociated molecule of phenol is in equilibrium with a small quantity of phenolated ions, which can take various isomeric forms depending on the movement of a pair of electrons away from the oxygen atom toward the aromatic nucleus:



Phenolated ions are stable (because of the three resonance formulas); this stability allows H^+ to move away and dissociate:



Acidity is a relative word; the dissociation constant of phenol ($1.3 \cdot 10^{-10}$) is much lower than that for acetic acid ($1.8 \cdot 10^{-5}$), which itself is a very weak acid. But if phenol is replaced with NO_2 groups, which really attract electrons in the ortho, meta and para positions, the result is a much higher acidity, for reasons already mentioned, up to values of around 10^{-1}, as in the case of 2,4,6-trinitrophenol, or picric acid:



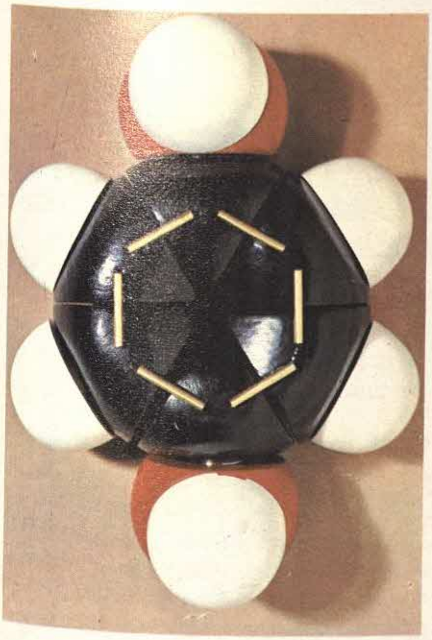
Phenol is much closer to alcohols in its readiness to form ethers with alcohols, and esters with acids. Another property of phenol is that it makes the benzene ring more reactive. While benzene is rather inert to substitution reactions, the presence of —OH makes the aromatic ring highly reactive, and this has the effect of activating the hydrogens in the ortho and para positions; these hydrogens can be substituted very easily. In other words, the hydroxyl positions its incoming substitutions ($-NO_2$, $-SO_3H$, $-Cl$, $-Br$, etc.) in the favorable ortho and para positions. The behavior of phenol on oxidization proves its greater reactivity; the conversion of benzene to phenol is very difficult, while phenol can easily be oxidized to polyhydroxylated compounds.

HOW PHENOL IS PROCESSED AND USED

So far, descriptions of the properties of the phenol class of compounds have been given in terms of the basic compound, phenol, since —OH is the group that gives it its characteristic appearance. Similarly, the manufacturing processes described below apply to the synthesis of phenol derivatives as well as to phenol.

HYDROQUINONE—This compound is found in several plants. Because of its strong reducing properties, hydroquinone is used in photographic development.

2

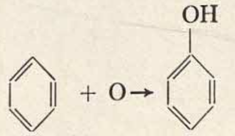


Phenol is obtained from coal tar; thus, the middle oil, which is the second fraction obtained in distillation (170°–230° C) (338°–446° F), contains mainly naphthalene and phenols. Since naphthalene crystallizes easily, separation is a simple matter, but phenols must be separated from the other elements by extraction with a solution of caustic soda. The result is sodium phenoxide, which, if it is made to react with mineral acids, produces phenol; the substance is then purified, first by distillation and then by crystallization.

Several factors, however, make the extraction of phenol from coal tar difficult. As a result, industrial synthesis is preferred—so much so that it has virtually put the natural method out of business, especially in the United States. The natural method involves time-consuming handling of the raw materials, particularly when the phenol content is low. In addition, the sulfur bases and foreign coloring compounds in phenol give it an unpleasant smell and color that are difficult to eliminate.

The industrial method makes more use of systems employing benzene as a starting point; phenol is produced either by direct oxidization or by substitution of other groups, such as SO_3H, Cl:

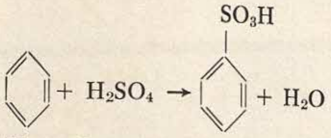
DIRECT OXIDIZATION



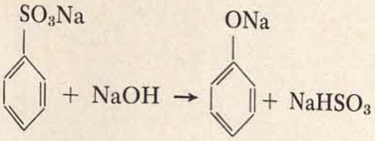
Benzene is resistant to oxidization. Because the oxidization reaction producing phenol gives relatively low yields, high temperatures and a high oxygen pressure are necessary to attack benzene. Once the phenol has been formed in the reaction mixture, it can be oxidized easily to produce multiple-substituted derivatives. If the process is taken too far, however, the ring is destroyed. This limits the use of the direct oxidization method and makes indirect methods preferable.

BENZENE SULFONATION AND HYDROLYSIS

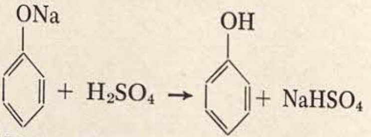
The benzene is first sulfonated with concentrated H_2SO_4 and then separated as a sodium salt from the reaction mixture:



The sodium benzenesulfonate is then fused with NaOH at 300° C (572° F):



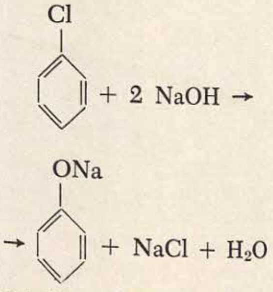
Mineral acids are used to neutralize the sodium phenate and thus liberate the phenol:



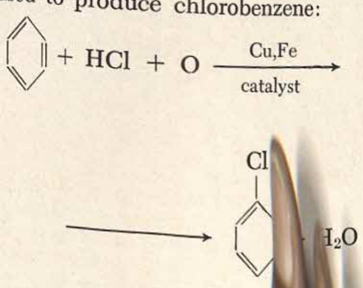
BENZENE CHLORINATION

The Dow process, as this method is called, is based on the hydrolysis of chlorobenzene with a solution of caustic soda at 300–350° C (572°–662° F) and 3,000 lb/in.[2]

The difficulty with this substitution reaction and therefore with the industrial application of the method, is the relatively strong bond between the substituents and the benzene ring:



A variation of this method is the regenerative or Raschig process, which is used to produce chlorobenzene:



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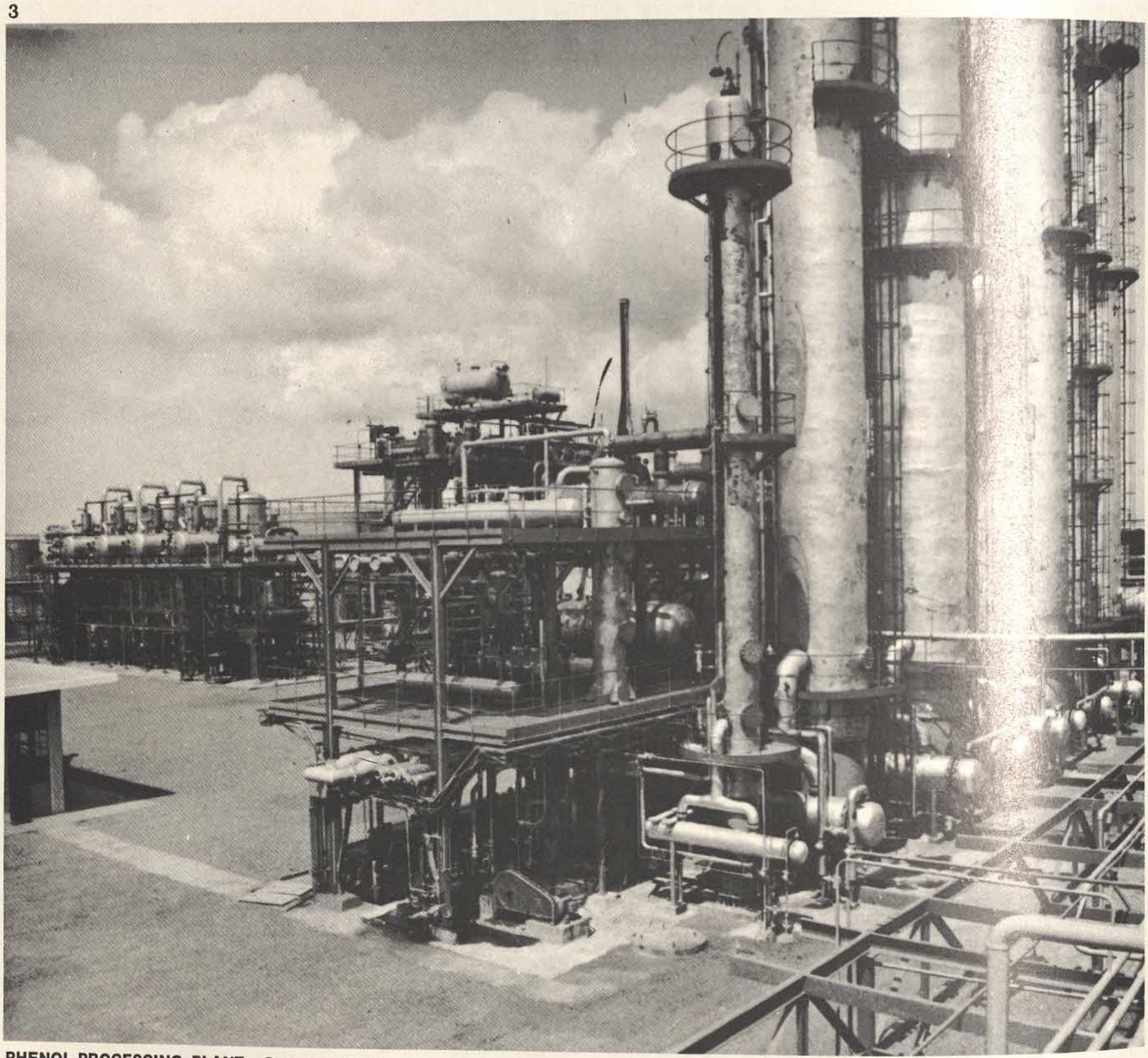
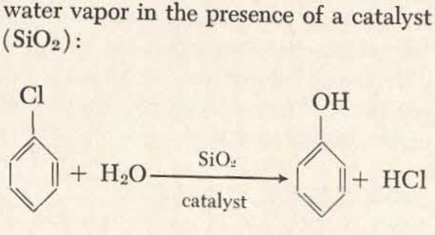


PHENOL-PROCESSING PLANT—One recently developed method for manufacturing phenol industrially uses cumene, which is obtained from benzene, as its starting point. Final products are acetone and phenol. Phenol is separated from the acetone by fractional distillation. The structures on the right are the phenol-acetone fractionating towers.

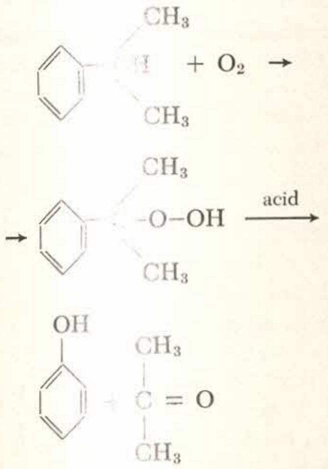
The chlorobenzene is hydrolyzed with water vapor in the presence of a catalyst (SiO_2):



This method allows maximum economy; the hydrochloric acid produced in the second reaction is used later to chlorinate more benzene, as is shown in the diagram illustrating the first stage of the process.

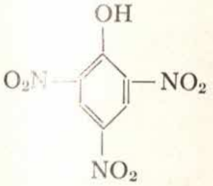
CUMENE PROCESS

This recently developed process is fast becoming the main source of phenol. If isopropylbenzene, or cumene, is oxidized with atmospheric oxygen, it forms a hydroperoxide which, when decomposed with water and acids, turns into phenol and acetone:



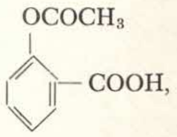
USES OF PHENOL

Phenol is condensed with formaldehyde in the presence of H_2SO_4 to produce Bakelite-type resins used for molding, laminating, adhesives, paints, etc. Phenol is also used in the synthesis of picric acid, the 2,4,6-trinitrophenol



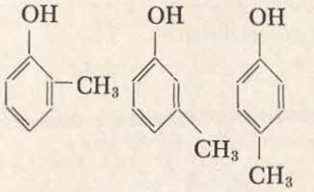
that is used in large quantities as an ammonium salt in the manufacture of explosives.

Because of its irritating action, phenol is no longer used as a disinfectant, but it is still used as a standard in evaluating other disinfectants and as a synthetic intermediate in the manufacture of salicylic acid, which has high antiseptic properties. Salicylic acid is used to produce acetylsalicylic acid (aspirin)



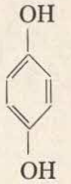
which is antipyretic and analgesic.

Phenol derivatives of particular importance include the methyl-substituted cresols. The three isomeric compounds

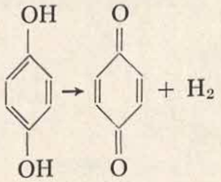


are found in the middle oils of coal tar and, when used industrially, are not usually separated from each other. Because their disinfectant power is higher than that of phenol, these isomeric compounds are often incorporated into soaps. The antiseptic properties of one such compound, creosote, make it useful in preventing deterioration of railway ties under the attack of organisms.

Of the dioxyphenols, the most important is hydroquinone

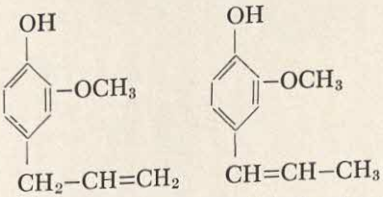


Easily oxidizable, hydroquinone is converted to benzoquinone or quinone:



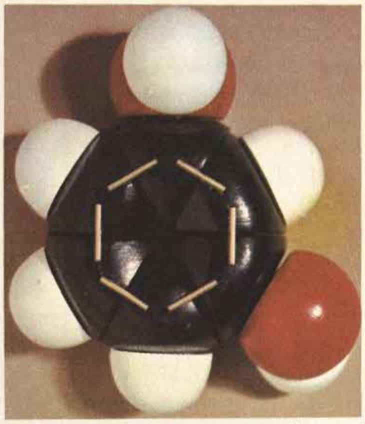
Quinones are compounds, ranging from yellow to red, that have lost their aromatic character but are highly unsaturated. The vivid colors in the tissues and organs of many molds, fungi, and other plants are due to the quinone compounds they contain. Hydroquinone is widely used as a photographic developer because of its properties as a high-speed reducing agent at room temperature.

Finally, many phenol derivatives are found in nature. Eugenol and isoeugenol,



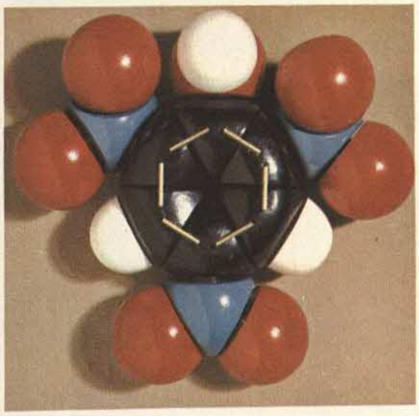
for example, are the essential oils of carnations and of nutmeg.

4



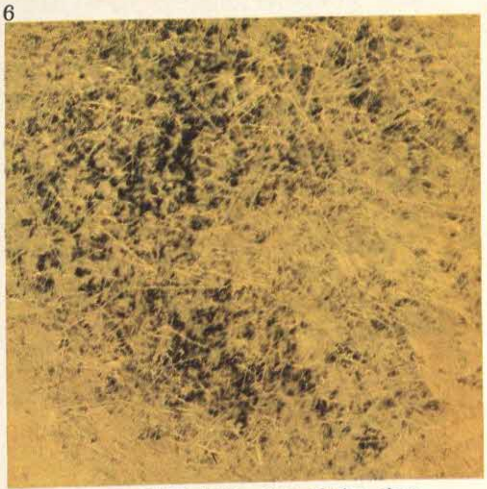
RESORCINOL—This compound, also called resorcin, is very reactive because of its two hydroxyls.

5



PICRIC ACID—Easily synthesized from phenol, picric acid is used in the manufacture of explosives.

6

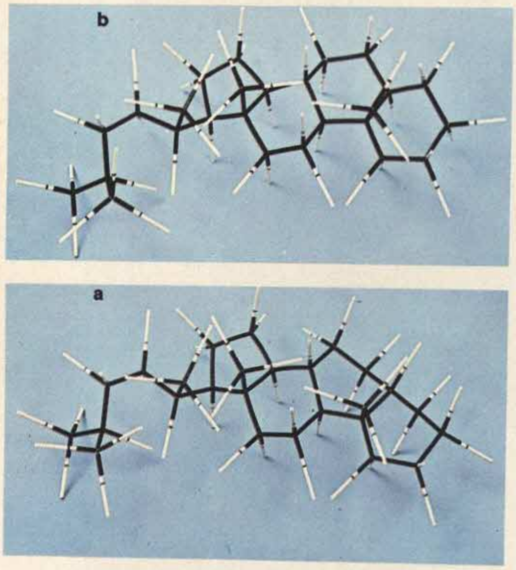


PICRIC ACID CRYSTALS—One of the characteristic features of picric acid is the manner in which it forms bright-yellow needle-shaped crystals.

THE STEROIDS | different substances with the same structural skeleton

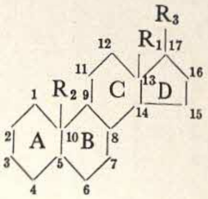
The steroids help control the body's utilization of water and minerals. Male and female sex hormones, cortisone, several forms of vitamin D, digitalis, and cholesterol are some well-known steroids. Medicinal uses of steroids include the treatment of arthritis and skin ailments as well as inhibiting immune response to foreign substances; it is thought that some steroids can inhibit cancer.

1

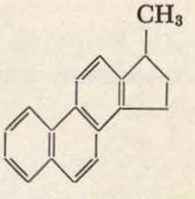


CHOLESTANE AND COPROSTAN—Molecular models of these hydrocarbons have the typical steroid structure, except for the fused cyclohexane rings. In cholestane (Illustration 1a), methyl and hydrogen at the fusion are on opposite sides of the molecule (*trans*-position), while in coprostan (Illustration 1b) the methyl and hydrogen are both on the same side (*cis*-position).

Steroids differ from one another only in the structure of their side chains and rings. All have the same basic molecular ring structure, called the cyclopentenophenanthrene system. Steroids contain essentially three nonaromatic rings with six carbon atoms, as well as one ring with five carbon atoms. The skeleton of the steroid molecule is:

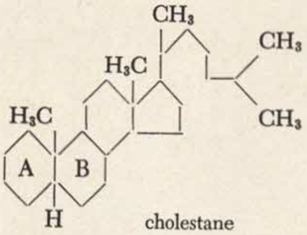


Selenium treatment provides a useful demonstration of this basic structure, giving rise to the aromatic hydrocarbon methyl cyclopenteno-phenanthrene, or Diels' hydrocarbon

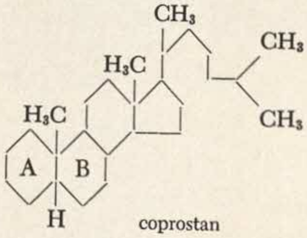


by eliminating also the substituent groups situated at the points where the rings are joined.

Steroids are so important to many bodily functions that they have been studied in great detail. Although side chains and rings may differ, all steroids can be related to two fundamental models of saturated hydrocarbons, cholestane and coprostan:



cholestane



coprostan

In cholestane, rings A and B are united in the configuration with hydrogen and methyl on opposite (*trans*) sides of the plane of projection; while in coprostan they are united in the *cis*-position. Most steroids display skeletons of the cholestane-type. The steroids, bile acids, sex hormones, and kidney hormones are of this type.

STEROLS

Sterols are characterized by a secondary hydroxyl function in position 3 and a double bond in position 5–6; thus, $R_1 = CH_3$, $R_2 = CH_3$, and R_3 is an aliphatic chain. They are crystalline solids found both in the free state and in esters with the higher aliphatic acids. Some are classified according to origin, as in zoosterols (animals), phyllosterols (plants), and mycosterols (fungi).

Sterols are extracted from those parts of natural fats that cannot be saponified (hydrolyzed by an alkali to form soap and glycerol). Some of the more significant sterols, which owe their importance to a close relationship with various vitamins, are cholesterol, stigmasterol, and ergosterol.

Cholesterol is the most important of the animal sterols. It is found in all living tissue to some degree; the solid part of the human brain contains 17 percent of

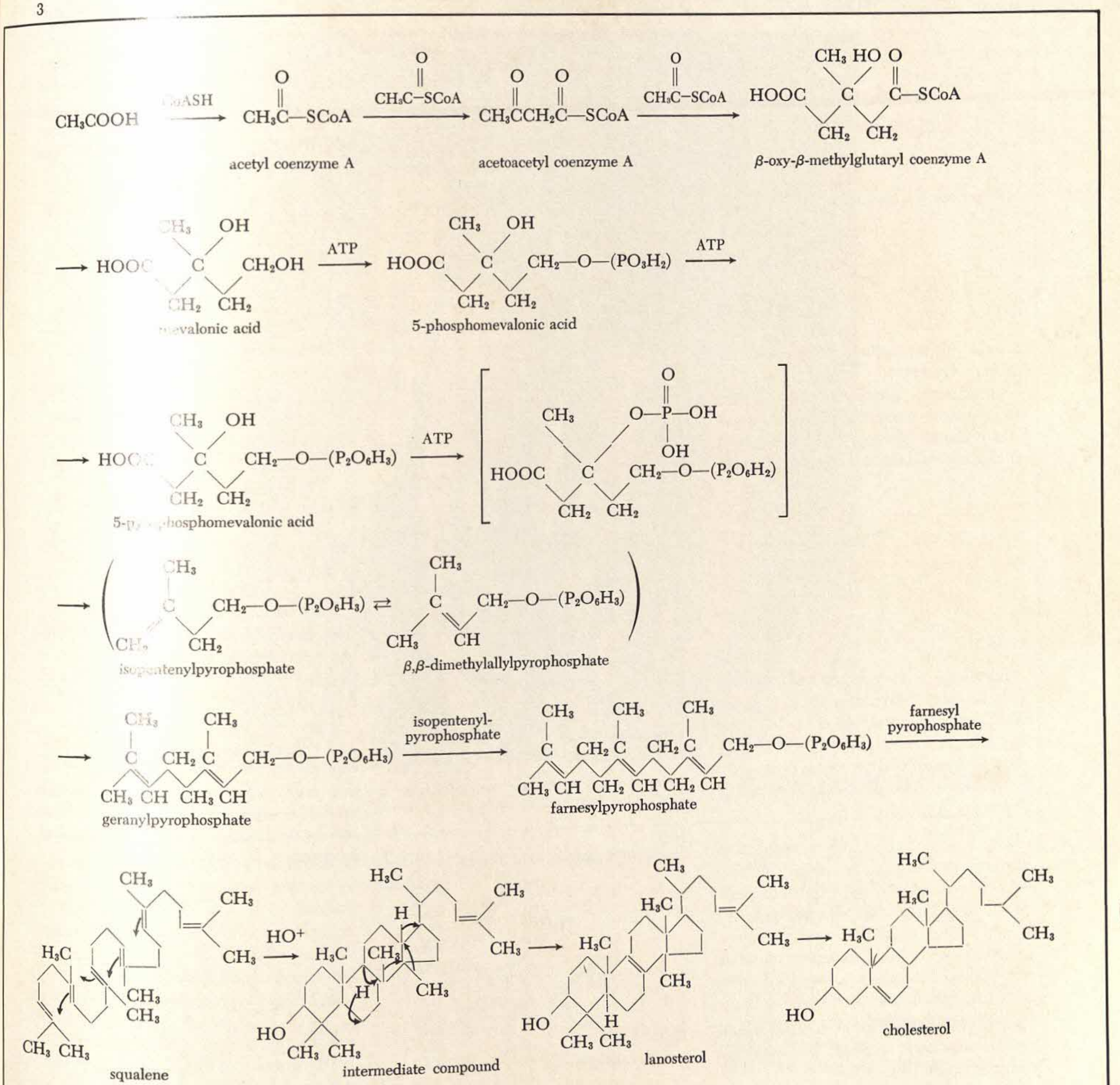
2a

2b

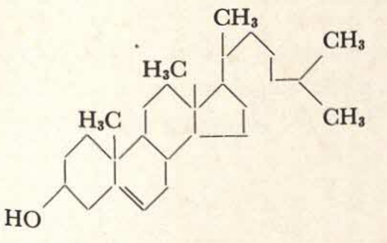
CHOLESTEROL—The word comes from the Greek word for bile and is found in gallstones in quantities between 75 and 99 percent. The substance is shown here as it appears to the naked eye (Illustration 2a), and under a microscope in polarized light (Illustration 2b).

BIOSYNTHESIS OF CHOLESTEROL—Animals can synthesize cholesterol as needed. The starting material is acetic acid, which is transformed, as isotopic analysis shows, into acetyl coenzyme A. The complete biosynthesis is shown in this illustration, with some terms omitted because this phase is barely known and not all intermediate compounds have been identified.

3



cholesterol. The structure is:

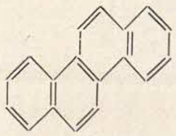


Steroid molecules contain several asymmetrical carbon atoms; the natural products are thus characterized by optical activity. Cholesterol has a specific optical activity of $(\alpha)_D = -36°$ (solvent is chloroform). Although the exact biological function is not clearly understood, it is known that cholesterol forms cholic acid and steroidal hormones in the body.

In recent years, cholesterol has been studied in connection with such circulatory disturbances as hardening of the arteries. Abnormal accumulations of cholesterol are associated also with other pathological conditions.

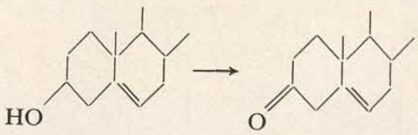
Commercial cholesterol (or lanolin) is obtained from the spinal marrow of cattle by means of solvent extraction. It is purified by transforming it into the dibromide, which can be crystallized using ethyl acetate.

In addition to its dehydrogenation into methyl cyclopenteno-phenanthrene, cholesterol also reacts to form chrysene:



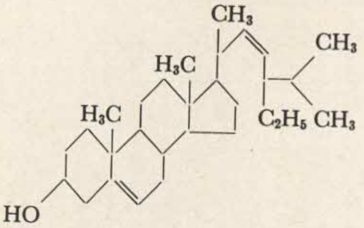
chrysene

cholestenone (a ketone):

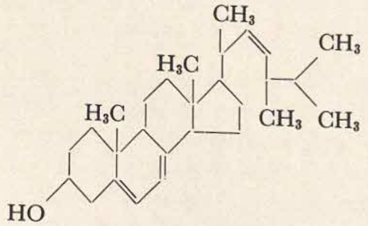


and the corresponding saturated hydrocarbon, cholestane.

Stigmasterol contains two carbon atoms and one more ring than cholesterol. It is obtained principally from soybean oil and is abundant in various vegetables.



Ergosterol is found in yeast together with its partial hydrogenation product, 5,6-dihydroergosterol. It is a solid fat that fuses at 174° C (about 345° F), displays an optical activity of $(\alpha)_D = -20°$, and contains three double bonds, two of which are conjugate:

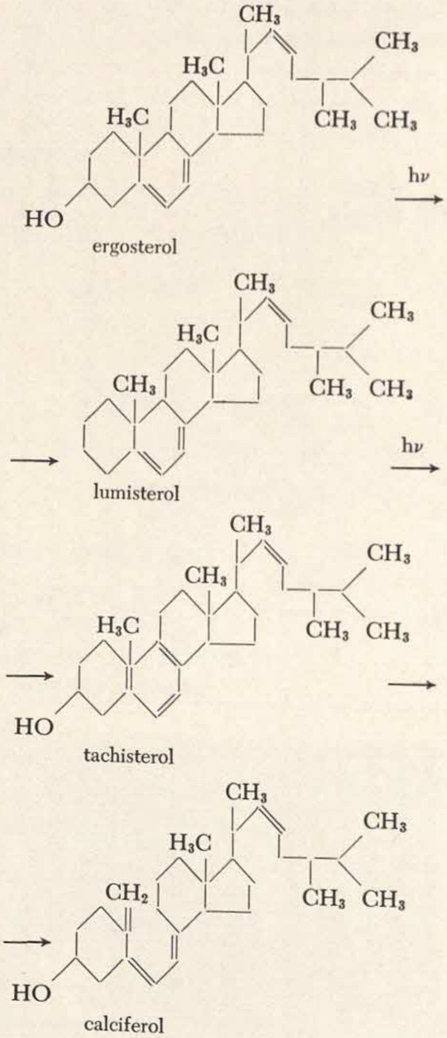


This sterol aroused great interest when researchers found it could be irradiated to form vitamin D.

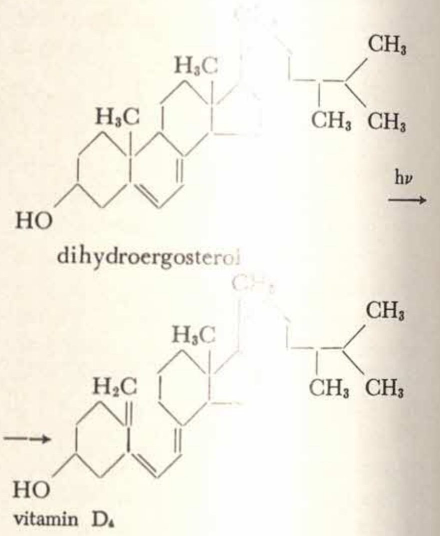
THE VITAMIN D GROUP

Various chemists noted in the 1920s that some foods acquired antirickets properties as a result of irradiation. It was later found that this was due to the formation of calciferol, or vitamin D_2, in the photochemical transformation of ergosterol from fats. The antirickets action of vitamin D_2 is probably due to its metabolic regulation of phosphates and calcium. It is a solid that fuses at 115 to 116° C (239 to 240.8° F) and has a specific optical activity of $(\alpha)_D = +82°$.

Vitamin D_2 does not have the typical structure of steroids; one of the rings is open. The formation of vitamin D_2 from ergosterol under irradiation is a complex reaction that includes various intermediate products:



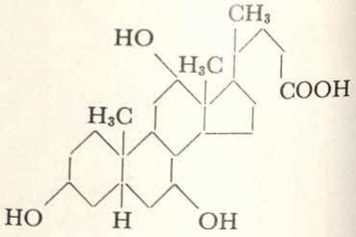
Other vitamins, notably vitamins D_3 and D_4, also display the antirickets property. A natural product found in the liver, vitamin D_3 is obtained by exposing 7-dehydrocholesterol to ultraviolet rays. The initial product is a cholesterol with two less hydrogen atoms and lateral chains that differ from ergosterol. Vitamin D_3 fuses at 82 to 85° C (179.6 to 185° F), and its specific rotational power amounts to +83° (in acetone). Vitamin D_4 is the result of the photochemical transformation of dihydroergosterol and its antirickets action is markedly weaker than that of vitamins D_2 and D_3. The formula is:



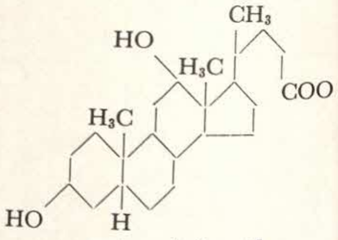
Vitamin D_4 differs from vitamin D_2 in that the double bond of the lateral chain has been eliminated.

BILE ACIDS

The bile acids have the same ring structure as coprostan and suggest a relationship with cholesterol. Experiments with marked compounds show that cholic acid can be obtained from the cholesterol of foodstuffs:

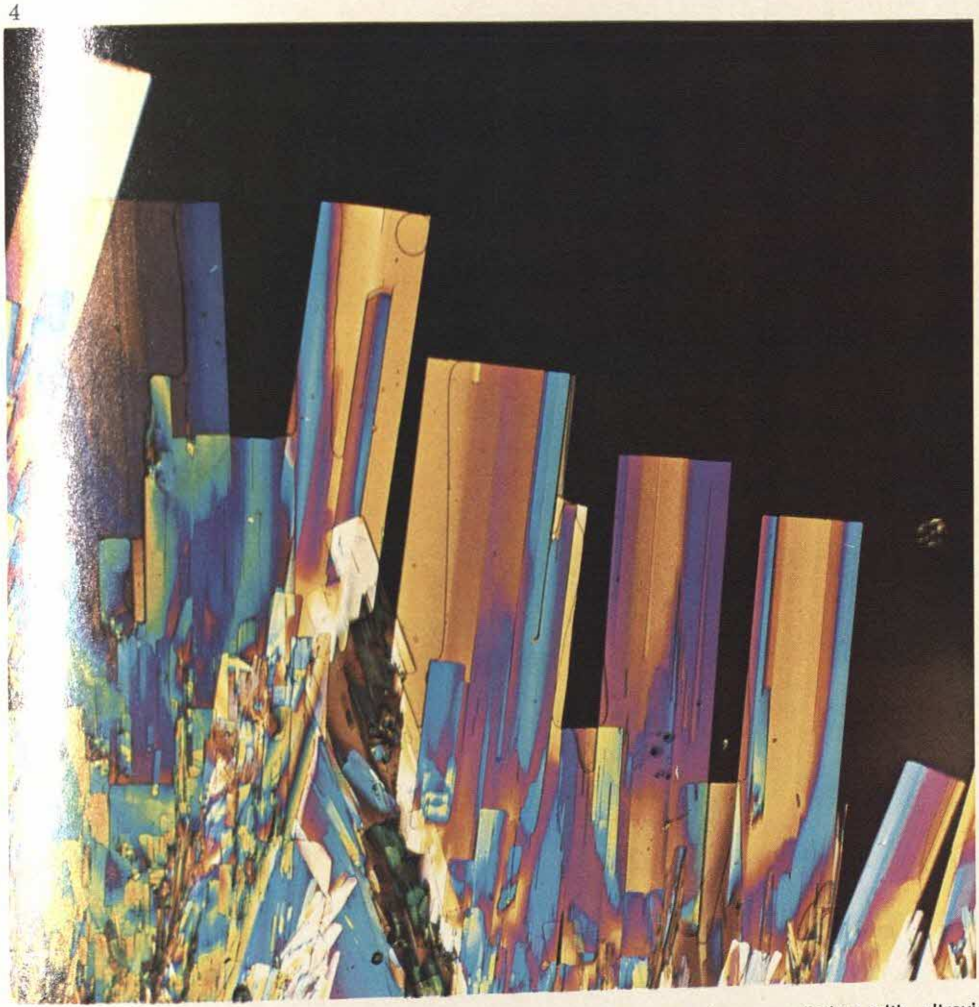


cholic acid



deoxycholic acid

4



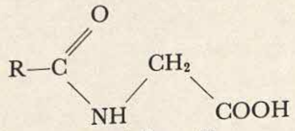
VITAMIN D_2—These vitamins are closely related to the steroids involved and are obtained by photochemical reaction. They are shown under a microscope in polarized light. On irradiation with ultraviolet light, ergosterol is converted to vitamin D_2.

In one process, potassium hydroxide is added to fresh ox bile. The mixture is then refluxed. Acidification of the alkaline liquor produces a solid mass, which is then washed; the dried crude acid is mixed with methanol. The mother liquor produces deoxycholic acid; the solid produces cholic acid.

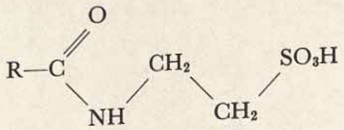
Both components, and others of the same class, exist in the bile in combined form as sodium salts (amides of glycine and taurine):

$H_2N{-}CH_2{-}COOH$	glycine
$H_2N{-}CH_2{-}CH_2{-}SO_3H$	taurine

The amide bond links the carboxyl group of the bile acid to the amine group of these two compounds. By using R—COOH as cholic acid, these compounds result:



glycocholic acid



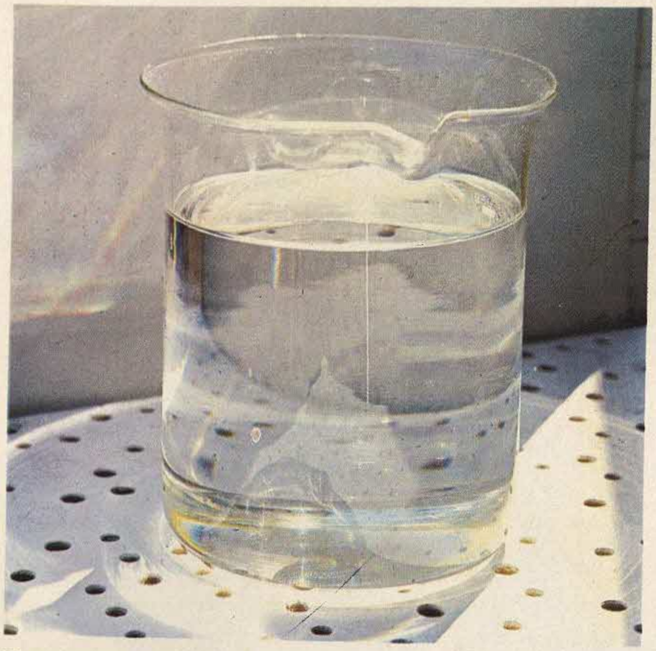
taurocholic acid

The free bile acids are obtained by alkaline hydrolysis of the peptide bonds. In the body, bile acids emulsify fats and assist digestion by certain enzymes. Moreover, bile acids form insoluble substances (high acid fats) that are more easily digested in the colloidal state. Choleic acid is one of these substances obtained by combining deoxycholic and palmitic acids. In conditions such as obstructive jaundice when sufficient amounts of bile do not reach the intestine, absorption of lipids is impaired.

The bile acids are obtained commercially from cattle bile. Deoxycholic acid is an important raw material for one industrial process for the production of cortisol and other related anti-inflammatory steroids. Cholic acid, the most abundant bile acid, occurring chiefly as the glycocholate bile salt, can be transformed into deoxycholic acid.

BENZENE | Kekulé's molecular dream

1



BENZENE—The colorless liquid in this beaker is benzene. It has a characteristic but not unpleasant odor. Its vapors, however, are extremely poisonous and, if inhaled continuously, will produce a profound and at times incurable condition known as aplastic anemia. The vapors affect the production of white and red blood corpuscles.

Organic compounds are so numerous and their characteristics so different that chemists have always found it useful to divide them into groups. One of these distinctions—a particularly helpful one—separates aliphatic and aromatic compounds. This distinction was first introduced about one hundred years ago. The meaning of these terms was originally as follows. Certain compounds of the methane series—paraffins with a high number of carbon atoms, for example—resemble fats and are used as lubricating agents. Moreover, even the true fats—that is, the esters of glycerine and fatty acids—are structurally related to methane. The term *aliphatic* (from the Greek *àlefair*, meaning "oil") came to refer to the derivatives of methane in general. Little by little, however, the term encompassed a growing number of substances in which hydrogen was present in relatively high proportions.

Other hydrocarbons, those isolated from resins or from essences, have a unique odor. All of these compounds were, therefore, called aromatics. Today the name persists even though it has no special significance.

The German chemist Friedrich August Kekulé von Stradonitz was the first to recognize that all aromatic compounds had at least six carbon atoms, and that their properties probably depended on a basic six-carbon-atom structural unit. The simplest aromatic compound is benzene, a hydrocarbon with six carbon atoms. Benzene was soon recognized as the fundamental aromatic hydrocarbon. Because it was regarded as being typical of aromatic substances, aromatic hydrocarbons were defined as compounds that have chemical properties similar to those of benzene.

Benzene, C_6H_6, is a colorless, limpid liquid with a characteristic odor. It boils at about 80° C (about 176° F) and solidifies at 5.5° C (about 42° F). At 25° C (77° F) its density is 0.874 and its refractive index 1.498. It is slightly soluble in water, more soluble in alcohol, completely miscible with ether, acetic acid, and carbon disulfide, and an excellent solvent for many substances. Benzene was isolated for the first time by the English physicist and chemist Michael Faraday in 1825. The structural formula of the molecule, however, remained completely unknown for many years after discovery of the compound. Establishing this structural formula was for a long time one of the most interesting lines of research in organic chemistry. This work intrigued many scientists because none of the proposed formulas succeeded in accounting for all of the experimentally derived properties of benzene. Analysis reveals that the benzene molecule consists of six carbon atoms and six hydrogen atoms.

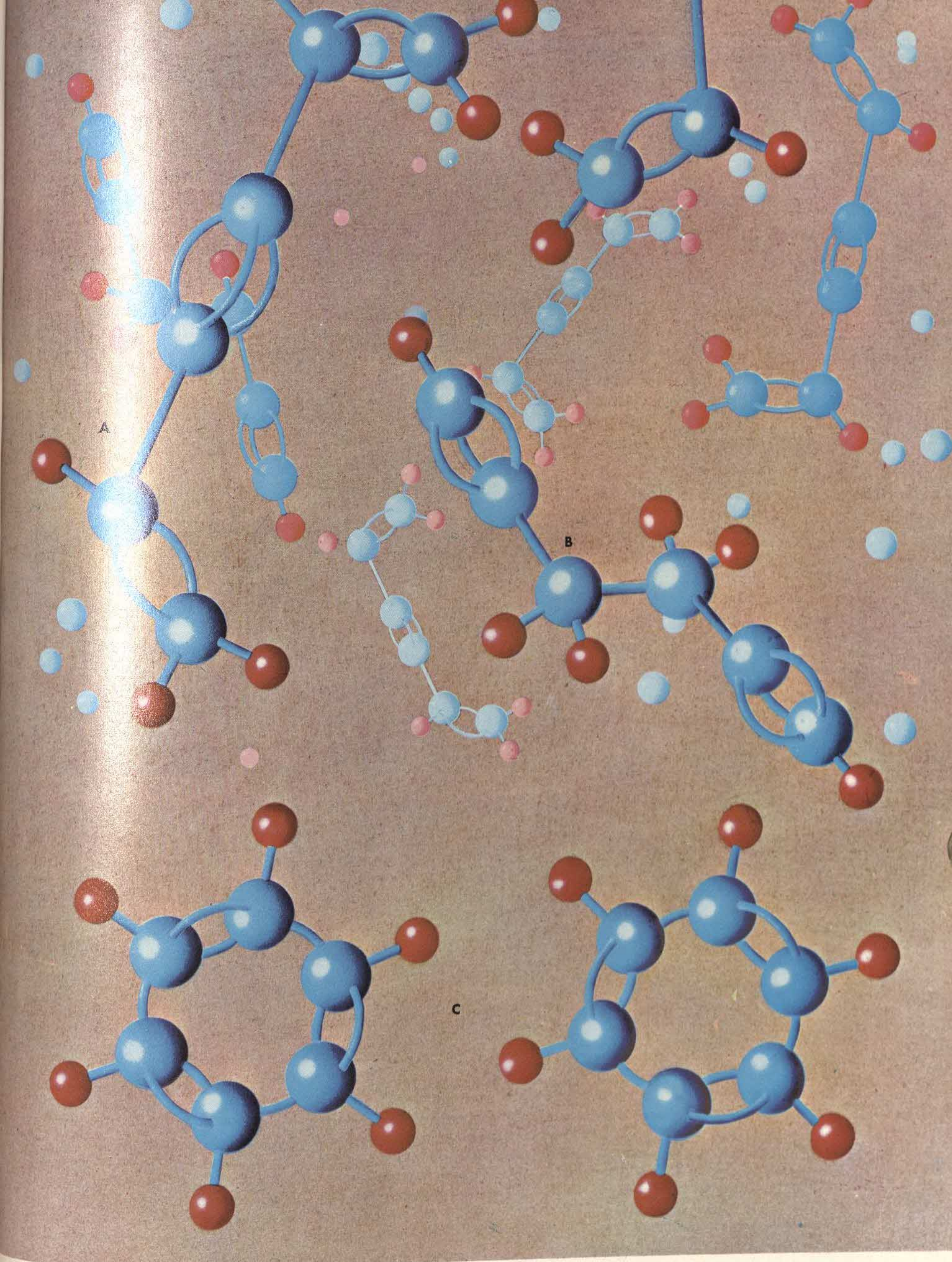
The relationship between the number of carbon atoms and the number of hydrogen atoms is one to one—the same as in the acetylene molecule, C_2H_2, which is an unsaturated compound. Unsaturated substances are highly reactive, however, while benzene and its derivatives are stable and much less reactive than such compounds as ethylene, acetylene, and derivatives that have an open chain.

On the basis of observations such as these, chemists immediately concentrated their attention on cyclic formulas, excluding linear formulas such as those shown in Illustrations 2a and 2b. A satisfactory model of the benzene molecule (Illustration 2c) was proposed by the chemist Kekulé in 1865.

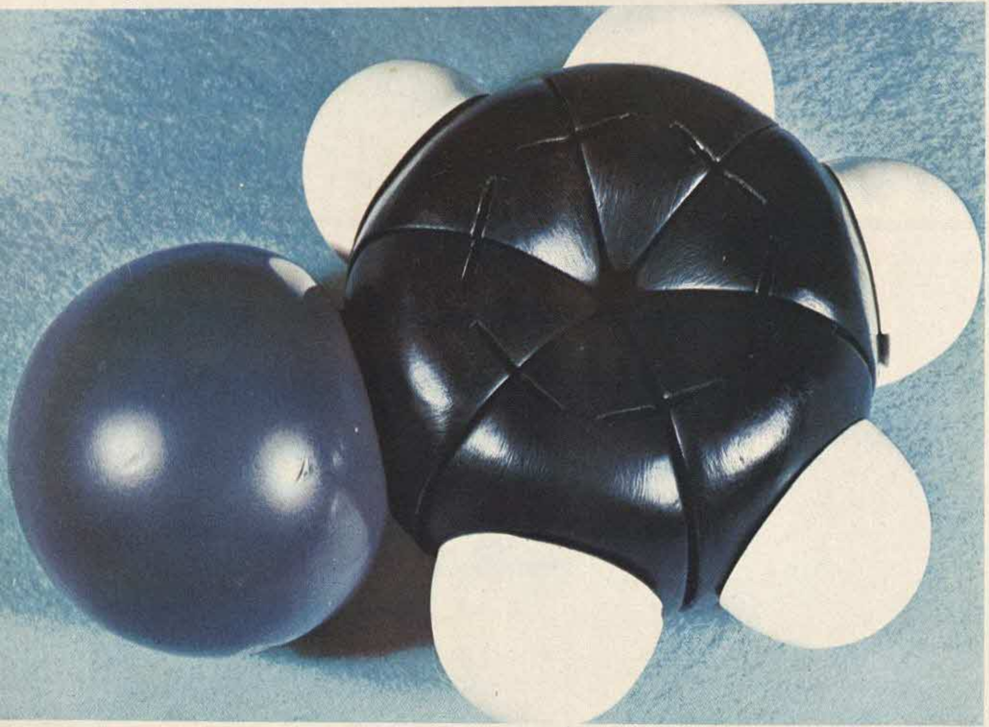
As Kekulé himself tells, the idea came to him in rather a curious manner. At the time that he was working intensely to resolve this problem, he happened to fall asleep in front of the fireplace after a very tiring day in the laboratory. He began to dream, and as he wrote later, "the atoms began to dance in front of my eyes, and the eyes of my mind succeeded in discerning structures of various conformations. Long strings of atoms, at times closely interconnected, twisted and wriggled like serpents. And then, quite suddenly, one of the serpents got hold of its own tail, forming a figure that danced mockingly in front of my eyes. I awoke as if I had been struck by lightning and

2

KEKULÉ'S DREAM — While working on the problem of the structural formula of benzene, Kekulé fell asleep in front of the fireplace. In a dream he saw the structures of many different molecules perform a dance before his eyes, twisting and wriggling like serpents. Suddenly one of these serpents got hold of its own tail and formed a ring structure. Linear structures such as those shown in Illustrations 2a and 2b were subsequently discarded. The hexagonal ring structure (Illustration 2c) was then adopted and confirmed by experiment.


A
B
C

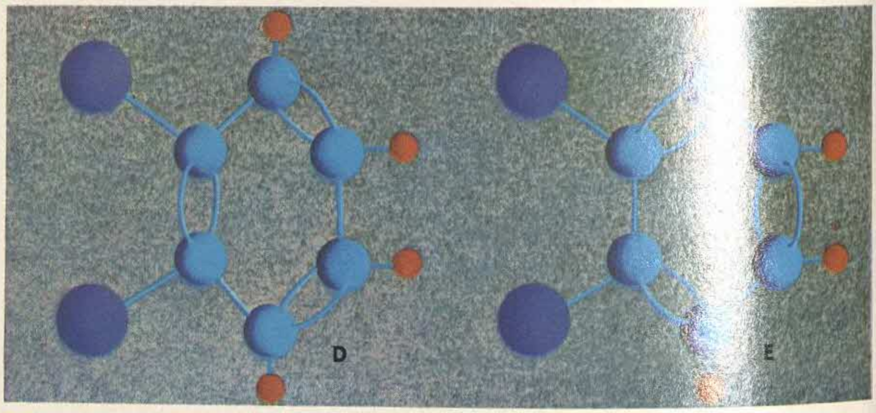
3



BROMOBENZENE—This compound is a substitution product of benzene; in the molecular model (Illustration 3) one of the hydrogen atoms has been replaced by a bromine atom. Since only one isomer of bromobenzene has been discovered, it follows that the six carbon-to-carbon bonds of benzene are equivalent. In other words, these six bonds must be arranged in a completely symmetrical manner.

***ORTHO*-DIBROMOBENZENE** — This substitution product of benzene has two bromine atoms *ortho* to one another; that is, bonded to adjacent carbon atoms (Illustration 4). If the bonds uniting the carbon atoms were not equivalent, but rather alternating single and double bonds, this compound should exist in two different isomeric forms. No isomers, however, have ever been observed in this compound.

4



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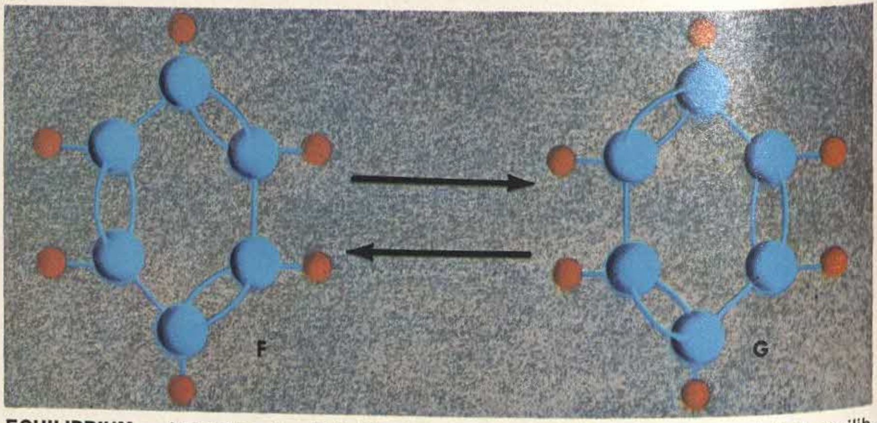

EQUILIBRIUM — According to Kekulé, the bonds in the benzene molecule resonate dynamically from one isomeric form to the other, thereby creating a kind of statistical equilibrium (Illustration 5). Such equilibrium must be extended to all of the derivatives of benzene.

spent the rest of the night working on the consequences of this hypothesis. . . One has to learn to dream."

Kekulé thus suggested that the structure of the benzene molecule might be a hexagonal ring in which the atoms of carbon are linked by an alternate succession of double and single bonds. This hypothesis is confirmed by systematic study of the substitution compounds of benzene; that is, of the compounds produced by substituting different atoms or groups of atoms for one or more hydrogen atoms. For example, there is only one methyl benzene (or toluene), $C_6H_5CH_3$, and only one bromobenzene, C_6H_5Br. No one has ever succeeded in isolating isomers of these compounds. If each product of a monosubstitution is unique, therefore, the inevitable conclusion is that the six hydrogen atoms of the benzene molecule are equivalent; that is, that they are arranged in a symmetrical pattern within the molecule. Three isomers are produced if a second substitution is accomplished. This constitutes yet another confirmation of the hexagonal form.

At this point, however, Ladenburg (who was then working on a different hypothesis) pointed out that the structural formula proposed by Kekulé did not resolve all the problems of the structure of benzene. In Kekulé's formula all of the identical atoms are structurally equivalent, but this is not the case with regard to the bonds between the carbon atoms. These bonds in the model consist of alternating single and double bonds, although experimental results show that the bonds, like the atoms, must be perfectly equivalent. For example, consider dibromobenzene with the two bromine atoms *ortho* to one another; that is, bonded to two adjacent carbon atoms. This compound should exist in the two forms shown in Illustration 4d and 4e. These two isomers, however, have never been observed. Kekulé thus altered his original hypothesis. He admitted that molecules such as those in Illustrations 4d and 4e were different, but went on

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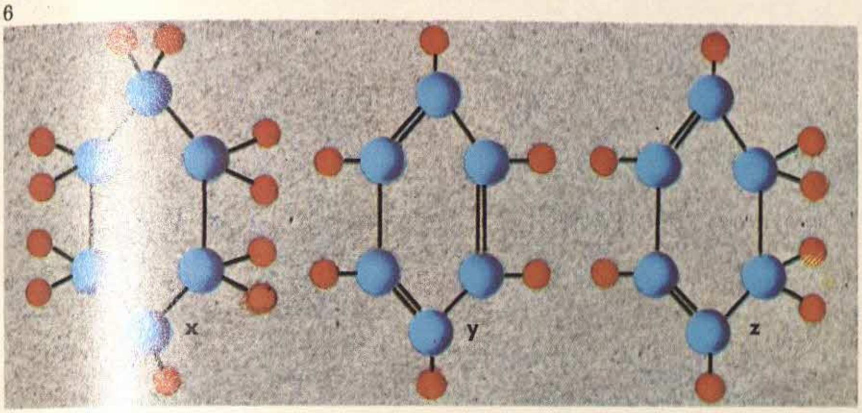
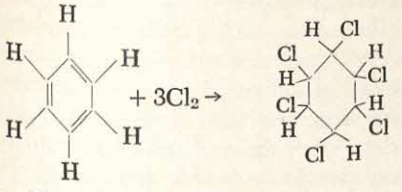


STABILITY—A molecule with resonating double bonds is more stable than another molecule in which the double bonds are not in resonance. Of the three compounds shown—cyclohexane x, benzene **y**, and cyclohexadiene **z**—cyclohexane is the most stable because it has no double bonds at all. Despite the larger number of double bonds in benzene, benzene is more stable than cyclohexadiene because its double bonds are in resonance, while those of cyclohexadiene are not.

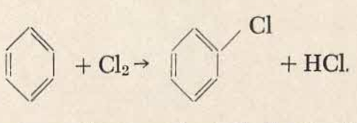
to say that they could nevertheless coexist because they were in a state of equilibrium. This means that the bonds in an individual molecule are sometimes as in Illustration 4d and sometimes as in Illustration 4e, with the molecule changing dynamically from one form to the other quite rapidly. In a sample of dibromobenzene, statistically there should be 50 percent molecules of one type and 50 percent molecules of the other type at any given instant.

Even if a mass of molecules made up of only one of the isomers were to be separated (an impossible task), the statistical equilibrium would be re-established very rapidly. This condition would prevent effective isolation of the two isomers. This type of equilibrium must be extended to all of the derivatives of benzene (Illustration 5).

It was not long before there were new criticisms of this simple description of the structure of benzene. Formulas such as those shown in Illustrations 5f and 5g should be more reactive than benzene actually is because of the double bonds. Kekulé's theory still did not explain this additional stability of benzene. If benzene, for example, were a substance of the ethylene type, additional reactions to the unsaturated bonds, including such reactions as



would take place. While such reactions do occur under suitable conditions, benzene lends itself more readily to substitution reactions that maintain the system of double bonds. For example,



These reactions are typical of saturated compounds such as the paraffins.

In spite of this objection and others put forward later, Kekulé's structure was used by chemists until World War II when application of the quantum theory finally solved the problem by considering the carbon-to-carbon bonds not as a succession of well-defined single and double bonds, but rather as a field of distribution of electrons. Benzene does not have the structures shown in Illustrations 5f and 5g, but rather a structure that is best described as a hybrid of these two. In the hybrid structure the bonds are considered to be an intermediate state between the single and the double bond. This makes all of the carbon-to-carbon bonds equivalent and gives them a saturation and stability that agree more closely with the properties of the molecule. This intermediate bond is called the resonance hybrid of the bonds shown in Illustrations 5f and 5g. In fact, the six carbon-to-carbon bonds in benzene are thought to be continuously in the hybrid state, and never alternately single and double.

The application of quantum mechanics has made possible a rigorous analysis of the phenomenon of resonance, although its existence had been intuitively suspected by organic chemists for some time previously. The theory of resonance is of the greatest importance in organic chemistry because it comes into play whenever a cyclic system of conjugate double bonds exists between atoms arranged in a plane. Resonance makes such molecules more stable than would be expected of a molecule with true double bonds. For example, consider the three compounds represented in Illustration 6.

Both benzene **y** and cyclohexadiene **z** can be converted to cyclohexane **x** by treatment with hydrogen in the presence of a platinum catalyst. From the amount of heat liberated in each reaction, it can be determined that the three double bonds in benzene are more stable than three of the type of double bonds present in cyclohexadiene. This is because there is no resonance in cyclohexadiene; the succession of conjugated double bonds is interrupted and does not extend throughout the ring.

Kekulé's formula suggests that the benzene molecule is hexagonal with sides of different lengths. The distance between two carbon atoms united by a single bond (1.54 Å) is greater than the distance between two carbon atoms united by a double bond (1.33 Å). According to resonance theory, however, the molecule should be a regular hexagon. X-ray diffraction studies have shown that the six bonds are equivalent and have a length of 1.40 Å, thus confirming that these bonds are intermediate between single and double bonds.

There has been no single and universally accepted way of representing the benzene ring in the chemical literature. A simple hexagon has been used for a long time. A diagram of the Kekulé structure has also been used (but always with the mental reservation that these diagrams are only approximations). Today there is a tendency to indicate the aromatic character of benzene and other cyclic molecules by means of a circle drawn inside the hexagon. This symbolizes the hybrid character of the bonds.

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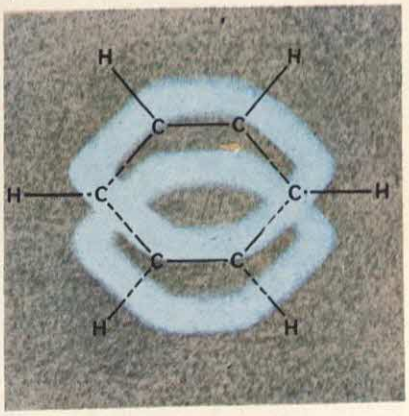
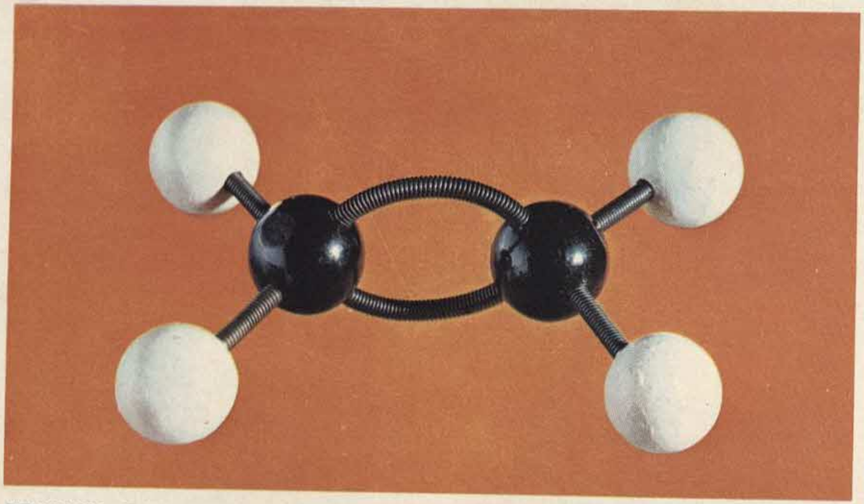


THE ELECTRON CLOUD—The carbon atoms of the benzene molecule are all in the same plane. This illustration shows the benzene ring with its electron cloud. To be precise, there are two electron clouds, one below and one above the carbon-atom ring. These clouds consist of electrons not involved in the carbon-to-carbon bonds. This structure has been confirmed by means of x-ray diffraction studies.

ETHYLENE AND ACETYLENE

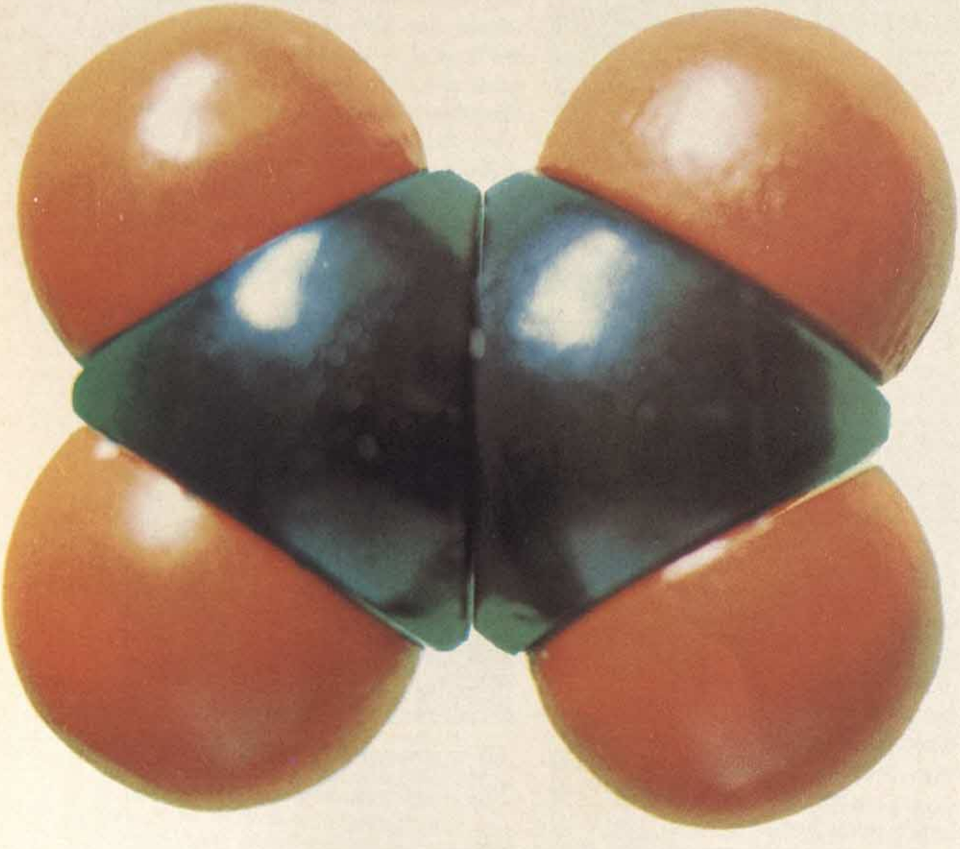
two important industrial raw materials

1a

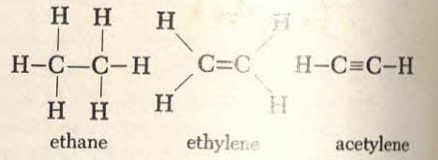


ETHYLENE—This model of the ethylene molecule (Illustration 1a) shows the double bond formed by two pairs of electrons shared by the two carbon atoms. The bonds between the carbon atoms and the hydrogen atoms, on the other hand, are single covalent bonds. The molecular model shown in Illustration 1b is a more accurate representation of the spatial arrangement of the atoms in ethylene.

1b



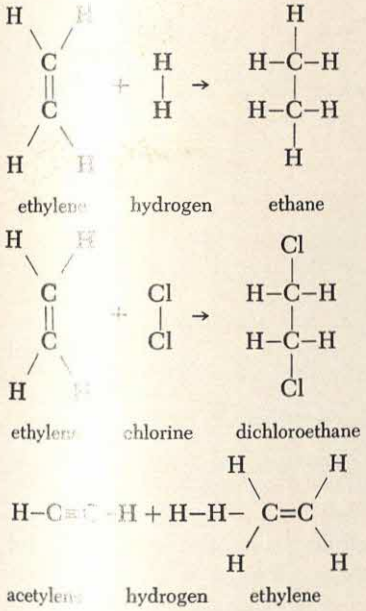
Organic compounds are extremely numerous (several hundred thousand are known). Moreover, in theory their number is infinite. Among the reasons for this unique multiplicity is the fact that two carbon atoms can bond together in three different ways—by a single bond, by a double bond, or by a triple bond. Thus, there are three different hydrocarbons with two carbon atoms: ethane (single bond), ethylene (double bond), and acetylene (triple bond):



The bond between the two carbon atoms of ethane is a typical covalent bond—the two atoms share a pair of electrons. In the double bond of ethylene, however, the two carbon atoms share two electron pairs. Since the carbon atom has a total of four valence electrons, each carbon atom in the ethylene molecule can bond to a maximum of two additional atoms (hydrogen in this case). This occurs because only two of its bonding electrons are still free. Three electron pairs are shared in the triple bond; each of the carbon atoms in acetylene can, therefore, bond to only one other atom. In this example, as with ethylene, the additional atom is hydrogen. It is obvious that the relationship between the two carbon atoms differs in the three types of bonds. In fact, the bond distances, that is, the distances between the two carbon nuclei, are different. They are 1.54 Å (Ångstroms) for the single bond ($1\ \text{Å} = 10^{-8}$ cm), 1.33 Å for the double bond, and 1.20 Å for the triple bond.

The distance between the carbon nuclei thus decreases as the number of bond electrons increases. If only single bonds exist in a compound (as in ethane), each carbon atom will be bonded to four other atoms. Under these conditions the compound is said to be saturated. Ethylene, acetylene, and their derivatives, on the other hand, are said to be unsaturated because one or more of their carbon valence electrons appear to be unused. In ethylene, for example, each carbon atom is bonded to only three other atoms, although it retains its tetravalent character.

A fundamental characteristic of unsaturated compounds is their pronounced reactivity. This makes it possible to transform them into various other organic products. The most characteristic reaction is addition of atoms or groups of atoms to the multiple bond. Some examples of such reactions are:



Ethylene is a colorless and combustible gas. Some natural gases found in America contain up to 20 percent ethylene; the quantity found in European natural gases, however, is always much lower. As is the case with almost all hydrocarbons, the most important source of ethylene is crude petroleum. The gas is produced by processes that split the more complex compounds into simpler molecules. The simplest laboratory method for preparing ethylene is the dehydration of ethyl alcohol by means of concentrated sulfuric acid.

During the First World War ethylene was used to prepare a powerful chemical weapon known as mustard gas. It was called mustard gas because the crude product in high concentrations has a smell similar to that of mustard. The gas has powerful blister-producing properties. It was used for the first time in July 1917, at Ypres in Flanders.

Ethylene is used in the artificial ripening of fruit and, mixed with oxygen, as an anesthetic. Its enormous industrial importance, however, stems from the fact that it is the starting material for a large number of products, particularly plastics. Among these important plastics are the vinyl resins, particularly polyvinyl chloride (PVC), which is widely used in building (dadoes, wall linings, window blinds), in upholstery work in railway carriages and automobiles, in clothing (raincoats), in electrotechnology (insulating materials), and in the packing industry. Acrylic resins are widely used for automobile stoplight reflectors, and acrylic fibers are used in the clothing industry in the form of synthetic fibers marketed under various proprietary names.

Another ethylene derivative is ethylene glycol, an interesting, colorless, and practically odorless liquid compound. Ethylene glycol is the major ingredient of almost all automobile antifreeze mixtures. The automobile industry is indebted to

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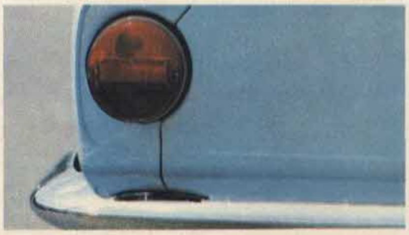
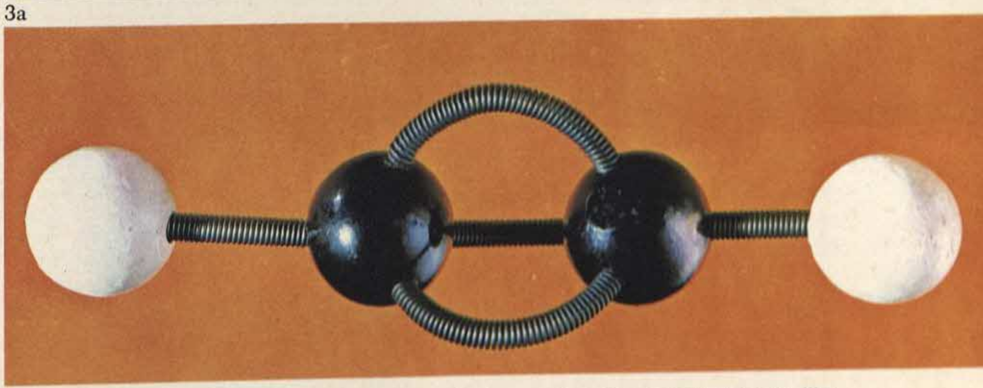


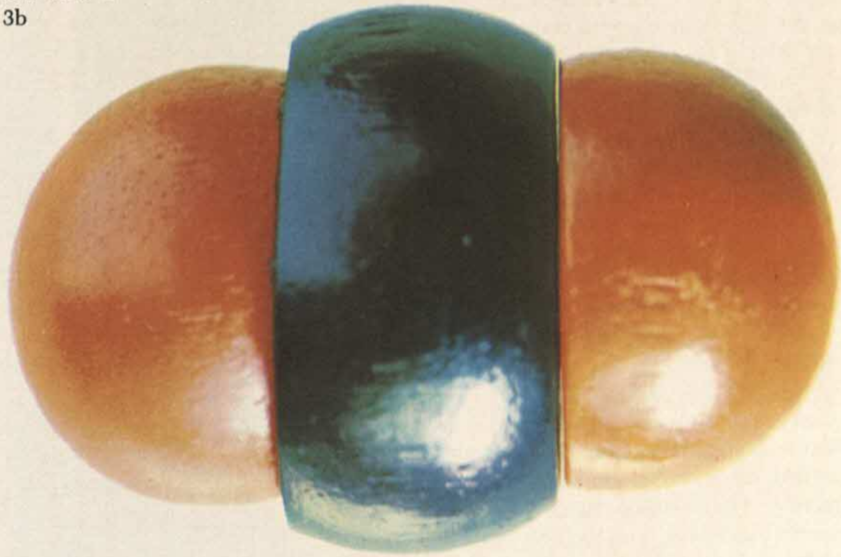
ACRYLIC RESIN—The reflectors of the rear lights of automobiles are made from a polymer that is derived from ethylene.

3a



ACETYLENE—The carbon atoms in the acetylene molecule share three electron pairs, thus forming a triple bond (Illustration 3a). The remaining valence electron of each carbon atom forms a single covalent bond with a hydrogen atom. The model shown in Illustration 3b better represents the spatial arrangement of the atoms in the molecule. Acetylene is a linear molecule—all of the atoms are found on the same straight line.

3b



A SPELEOLOGIST'S HELMET—The flame burning at the front of the helmet is fueled by a small acetylene generator. The cylinder of this generator contains calcium carbide at the bottom and water in the upper part. Drops of water are allowed to fall onto the calcium carbide by means of a screw-controlled valve, thus regulating the rate at which the acetylene is produced.

4

ethylene for another widely used product —tetraethyl lead. This compound is one of the most widely used antiknock additives for gasoline, although it is now under attack as a polluter of the atmosphere. Finally, polyethylene, a polymer of ethylene, has assumed tremendous industrial importance during the last decade. Initial applications of polyethylene were based on its exceptional insulating properties. It is thus widely used in electrical circuits. In fact, the availability of polyethylene played an important part in the construction of the first radar installations. Polyethylene's resistance to corrosive inorganic chemicals makes it an ideal material for pipes and conduits in chemical plants. In some countries polyethylene pipes have even been used on a large scale for water mains.

Acetylene is also a colorless gas. In the pure state it is practically odorless. Commercial acetylene, however, generally has an unpleasant odor as a result of contamination by phosphine and hydrogen sulfide. Acetylene burns with a highly luminous flame. The flame is also quite smoky, probably because the hydrocarbon is broken down into finely divided carbon particles that do not burn completely. The classical method for preparing acetylene consists of reacting water with calcium carbide. The calcium carbide is obtained from carbon and lime in special furnaces at temperatures of the order of 2,500 to 3,000° C (4,532 to 5,432° F). Although this old process is still widely used, a method based on the partial oxidation of methane has become more popular during the last few years.

Acetylene was widely used for illumination purposes (carbide lamps) before the invention of the electric light bulb. Until a few decades ago, for example, the front lights of bicycles included a small acetylene generator, that is, a small metallic receptacle containing calcium carbide into which water could be dropped through a valve.

Although acetylene liquefies readily, it is quite explosive in the liquid state, and thus would be difficult to store in cylinders. This problem has been solved by storing the acetylene at moderate pressure (12 atmospheres) in cylinders containing porous masses of asbestos soaked in acetone. Acetylene is highly soluble in acetone (1 liter of acetone will dissolve up to 300 liters of acetylene). Large quantities can, therefore, be stored in a comparatively small space.

Oxyacetylene torches with their cylinders of oxygen and acetylene are used in almost every mechanical workshop. The flame produced by this type of torch can exceed 3,000° C (5,432° F), and so is used for cutting and welding metals.

Acetylene, like ethylene, is the starting material for the manufacture of a large number of useful products. These include ethyl alcohol, acetone, and acetic acid, as well as synthetic fibers and rubber.

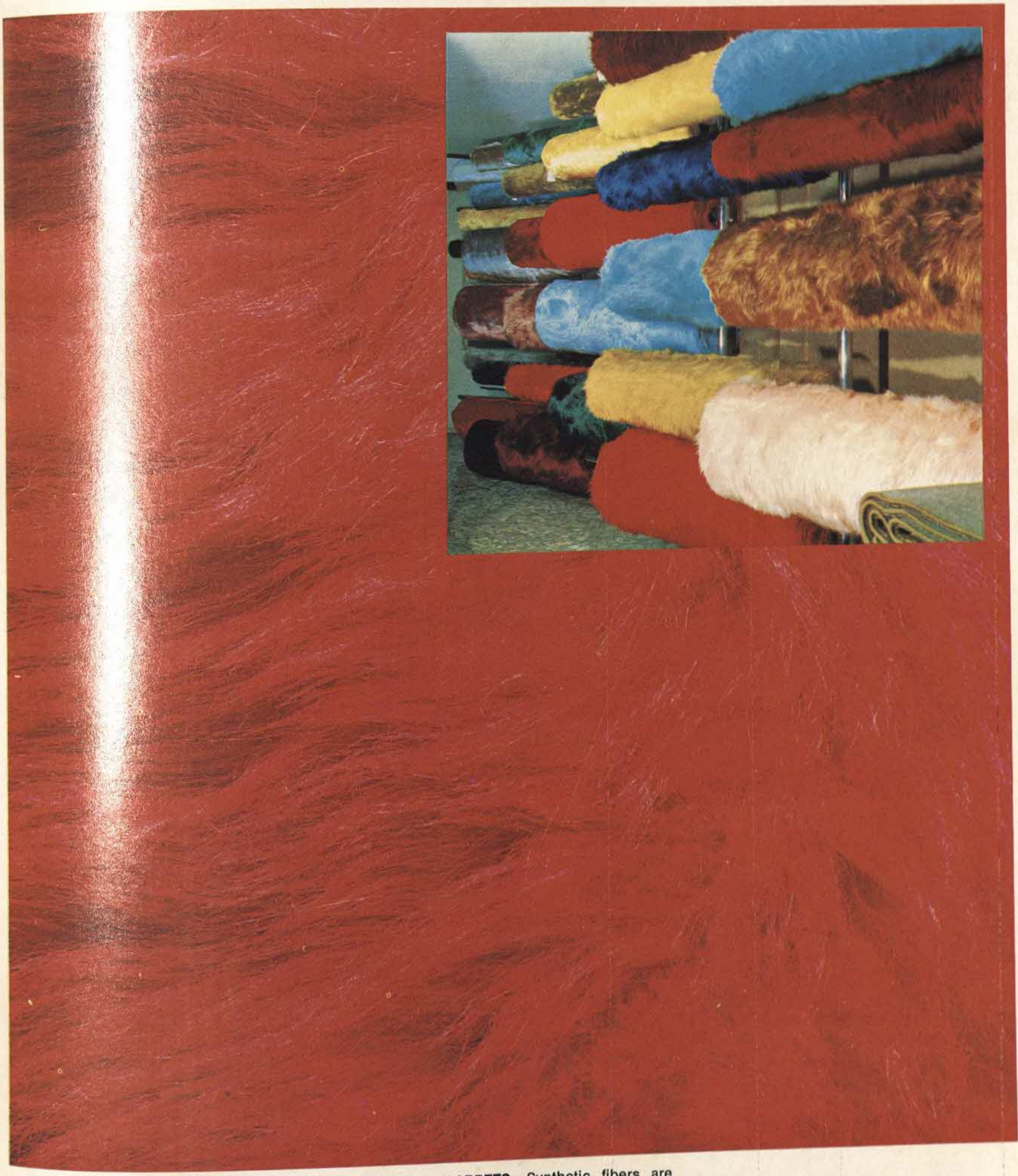
Ethylene and acetylene are thus of great importance because they are typical compounds with double and triple bonds.

THE OXYACETYLENE TORCH—This torch is supplied by separate streams of oxygen and acetylene, and produces a very hot flame that can easily exceed 3,000° C (5,432° F). Hence it is used for cutting and welding metals.

5

6

AN ETHYLENE POLYMER—This organic substance, seen here in the crude state, is a polymer derived from ethylene. It has a large number of practical applications.



SYNTHETIC CARPETS—Synthetic fibers are firmly entrenched in modern life. They are soft, strong, and warm, and lend themselves to a wide variety of uses.

THE PARAFFINS | saturated hydrocarbons

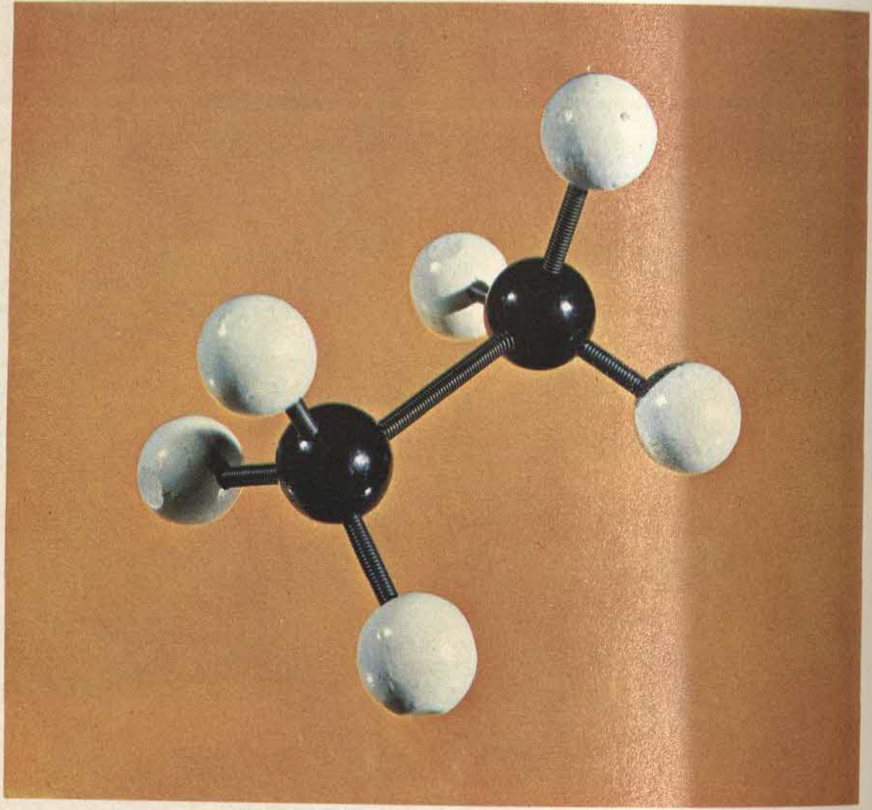
Because of their low reactivity—that is, because they show little tendency to react chemically when they contact other substances—saturated hydrocarbons deserve the name of paraffins. This term is derived from the Latin *parum affinis*, meaning "slightly kindred." The term "saturated" means that all the carbon valences in a molecule are saturated with hydrogen atoms, thus reaching a high ratio of hydrogen to carbon atoms. Paraffin hydrocarbons, which are also called alkanes, are characterized by single bonds between adjacent carbon atoms. Single bonds consist of a single electron pair.

An extraordinarily high number of saturated hydrocarbons exist because the carbon atoms link up to form chains. No maximum has been established for the number of carbon atoms that may link up to form a chain. Molecules with 70 directly linked carbon atoms have been synthesized; there is no reason to believe that even longer chains would not be stable. The carbon atoms in paraffins link up by sharing a pair of bonding electrons. Those carbon atoms not involved in forming the carbon chain, however, are saturated with hydrogen atoms.

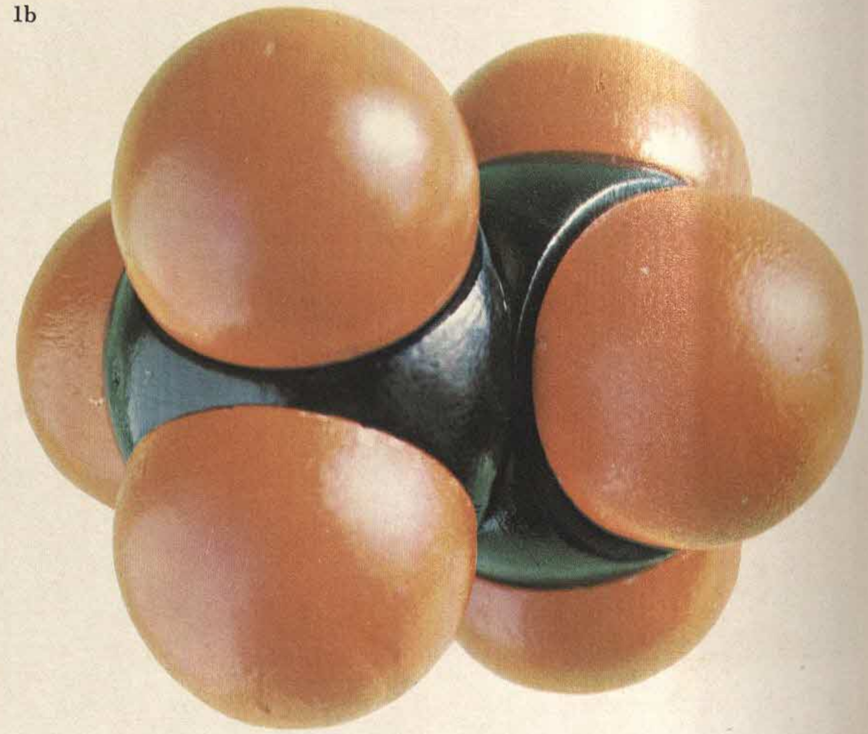
A typical paraffin, by definition, consists of a molecular chain containing n carbon atoms, each of which is bonded to two hydrogen atoms, with the exception of the initial and terminal carbon atoms, which are bonded to an additional hydrogen atom. Such molecules are described by the general formula C_nH_{2n+2}. That is, for every carbon atom the number of hydrogen atoms equals two times the number of carbon atoms plus two. The carbon chain of a paraffin molecule can be represented in space by a zigzag line. This orientation in space is a logical consequence of the fact that carbon atoms in paraffin molecules form bonds that point toward the vertices of a tetrahedron. Such bonds form an angle of 109° 28′ with each other. Moreover, the average distance between carbon atoms in paraffin molecules is 1.4 Angstroms (10^{-8} cm = 1 Å).

The simplest compound of the paraffin series is methane (CH_4); all other paraffin molecules are homologs. Such a homologous series is made up of compounds of the same type, all of which agree in composition to a general formula. In the paraffin series each compound differs from the preceding one by a $-CH_2$ group.

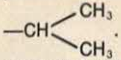
1a



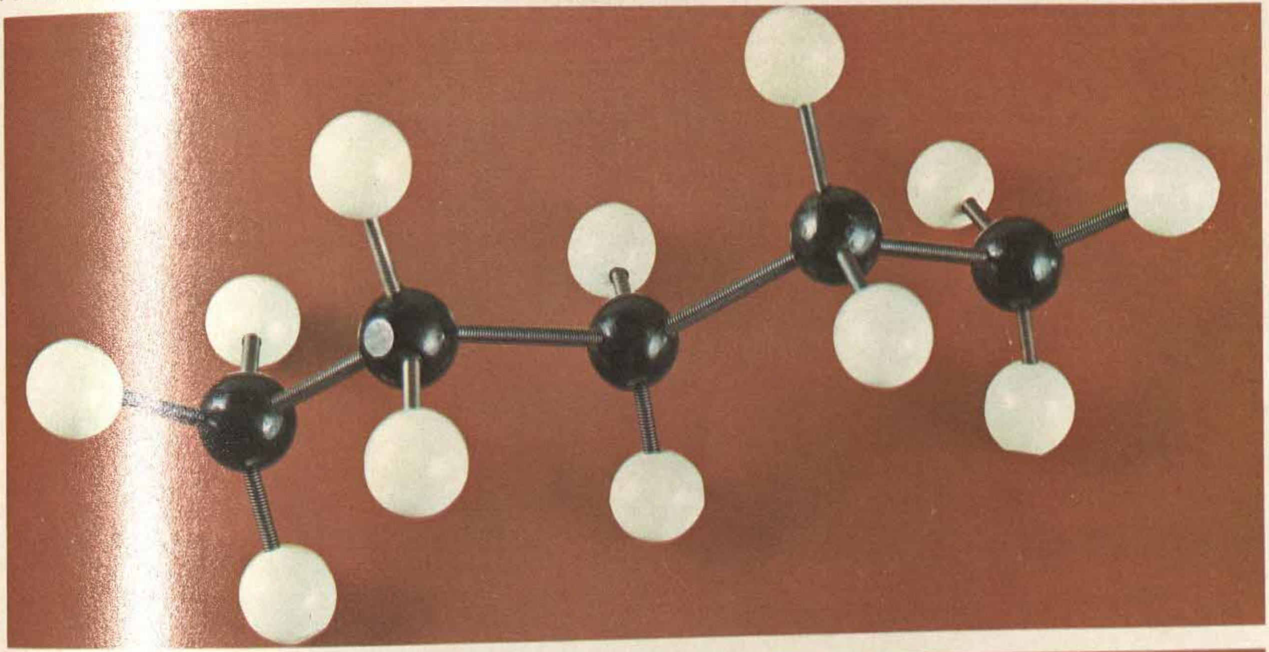
1b



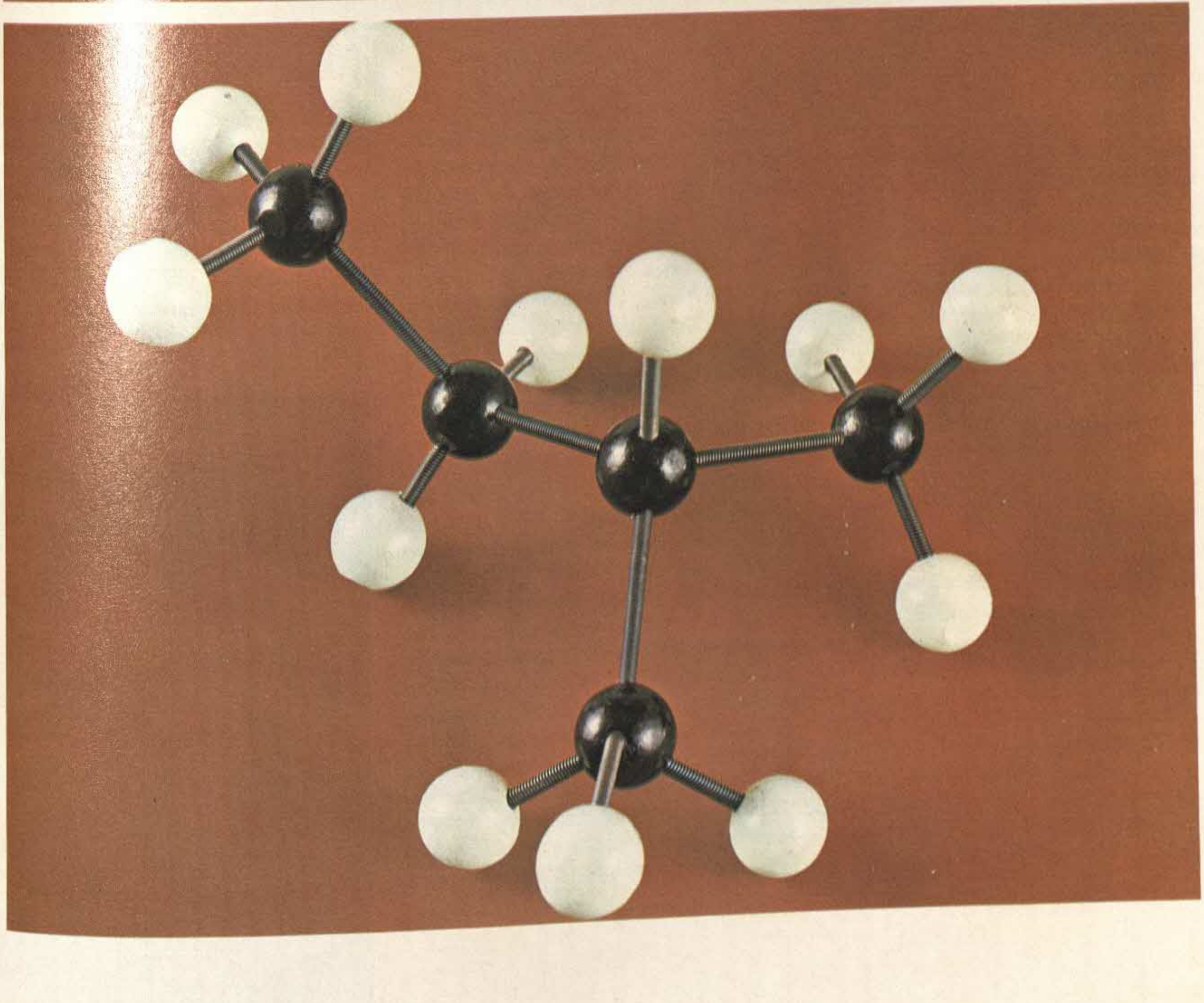
ETHANE—The molecule of this hydrocarbon (Illustration 1a) contains two carbon atoms (black) and six hydrogen atoms (white) joined by single bonds. The model shown in Illustration 1b provides a better idea of the molecule's structure. In this model the relative sizes of the atoms are shown more correctly.

ISOMERISM — The compounds shown here have the same number of carbon and hydrogen atoms, that is, the same basic formula: C_5H_{12}. They differ, however, in the way that the carbon atoms are arranged differently in space. Note the linear chain in Illustration 2a and the branched chain in Illustration 2b. Linear chain molecules are said to be normal (the illustration shows normal pentane, n-pentane). The branched chain in Illustration 2b is called isopentane because of the presence of the group  $-CH\begin{matrix} \diagup CH_3 \\ \diagdown CH_3 \end{matrix}$. Molecules containing this group have the prefix iso-.

2a



2b



3

PARAFFIN—This substance is commonly known as paraffin. It is a mixture of solid high molecular weight hydrocarbons in the form of large linear chain molecules. Paraffin is obtained by the distillation of petroleum.

The first four compounds of the paraffin series are methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and butane (C_4H_{10}). Molecules higher in the series are named in terms of Greek and Latin prefixes derived from the number of carbon atoms in the molecule, plus the suffix -ane, which applies to saturated hydrocarbons in general. Examples are pentane (5 carbon atoms: C_5H_{12}), hexane (6 carbon atoms: C_6H_{14}), and so forth.

ISOMERISM

Starting with the fourth paraffin molecule, butane (C_4H_{10}), more than one molecular structure becomes possible for the same basic formula. These differing structures are called isomers. The number of isomers increases noticeably as the number of carbon atoms in a molecule increases. Isomerism, which comes from the Greek *isos* meaning "equal," and *meros,* meaning "part," occurs when two or more compounds with the same basic formula differ because their atoms are arranged differently in space. The phenomenon of isomerism is based on the fact that the carbon atoms of a paraffin molecule may form branched as well as linear chains.

A molecule consisting of a linear chain is said to be normal. For example, normal pentane, abbreviated n-pentane, contains five carbon atoms linked together in a straight chain. In the case of paraffin hydrocarbons, the greater the number of carbon atoms, the greater the number of possible isomers. For example, there are 9 heptanes, 18 octanes, 35 nonanes, and so forth.

PARAFFINS IN NATURE

Saturated hydrocarbons are fairly widespread in nature. Methane and other paraffin molecules with only a few carbon atoms are found in naturally occurring gases. These gases are found particularly in petroleum-bearing strata, and occasionally in other deposits such as potassium salt mines.

A typical fuel gas coming from deposits of this type contains about 85 percent methane, 9 percent ethane, 3 percent propane, 1 percent butane, and the rest nitrogen. Petroleum is another natural product containing saturated hydrocarbons. Petroleum from Pennsylvania is especially rich in paraffin molecules. It consists of a mixture of hydrocarbons whose carbon-atom number varies from 1 to 30 or 40. On the other hand, petroleum from the Caucasus region is rather lacking in these compounds. Mineral waxes such as ozokerite, however, consist primarily of a mixture of high molecular weight paraffins. Such compounds originate from petroleum paraffins by means of polymerization; that is, by smaller molecules linking up to form high molecular weight compounds. These are found, for example, at Baryslaw in Galicia. Saturated hydrocarbons are also found in plant essences. Normal heptane, for example, is easily extracted from the turpentine found in two species of American pines—*Pinus jeffreyi* and *Pinus sabiniani.* Small percentages of other saturated hydrocarbons with high molecular weights are found in beeswax, particularly heptacosane ($C_{27}H_{56}$) and hentriacontane ($C_{31}H_{64}$).

PHYSICAL PROPERTIES

The first four paraffins (methane CH_4, ethane C_2H_6, propane C_3H_8, and butane C_4H_{10}) are gaseous at room temperature. Butane boils at about 0° C (32° F). Pentane (C_5H_{12}) to the C_{16} compound are liquids. The higher members of the series are solids. Both boiling point and melting point increase as the number of carbon atoms increases. The difference between the boiling or melting points of two successive compounds decreases as molecular weight increases. An increase of one $-CH_2$ group, for example, represents an increase of about one sixth of the molecular weight going from C_5 to C_6; the corresponding difference in boiling points is 33° C. In moving from C_{18} to C_{19}, however, the addition of one $-CH_2$ group represents an increase of about one nineteenth of the molecular weight; in this case the corresponding difference in boiling point is only 13 C° (23.4 F°).

This general rule applies to linear paraffin molecules. Branched paraffins, however, generally boil at lower temperatures than linear paraffins with the same number of carbon atoms. In fact, with branching, the shape of the molecule tends to become somewhat spherical. As a result, surface area decreases and intermolecular forces become weaker. These weaker forces break at lower temperatures, accounting for the lower boiling points. The specific gravity of paraffin compounds increases slowly with increasing molecular weight. Paraffins are extraordinarily difficult to dissolve in water. In common organic solvents, however, they are highly soluble. This solubility diminishes as weight increases.

CHEMICAL PROPERTIES

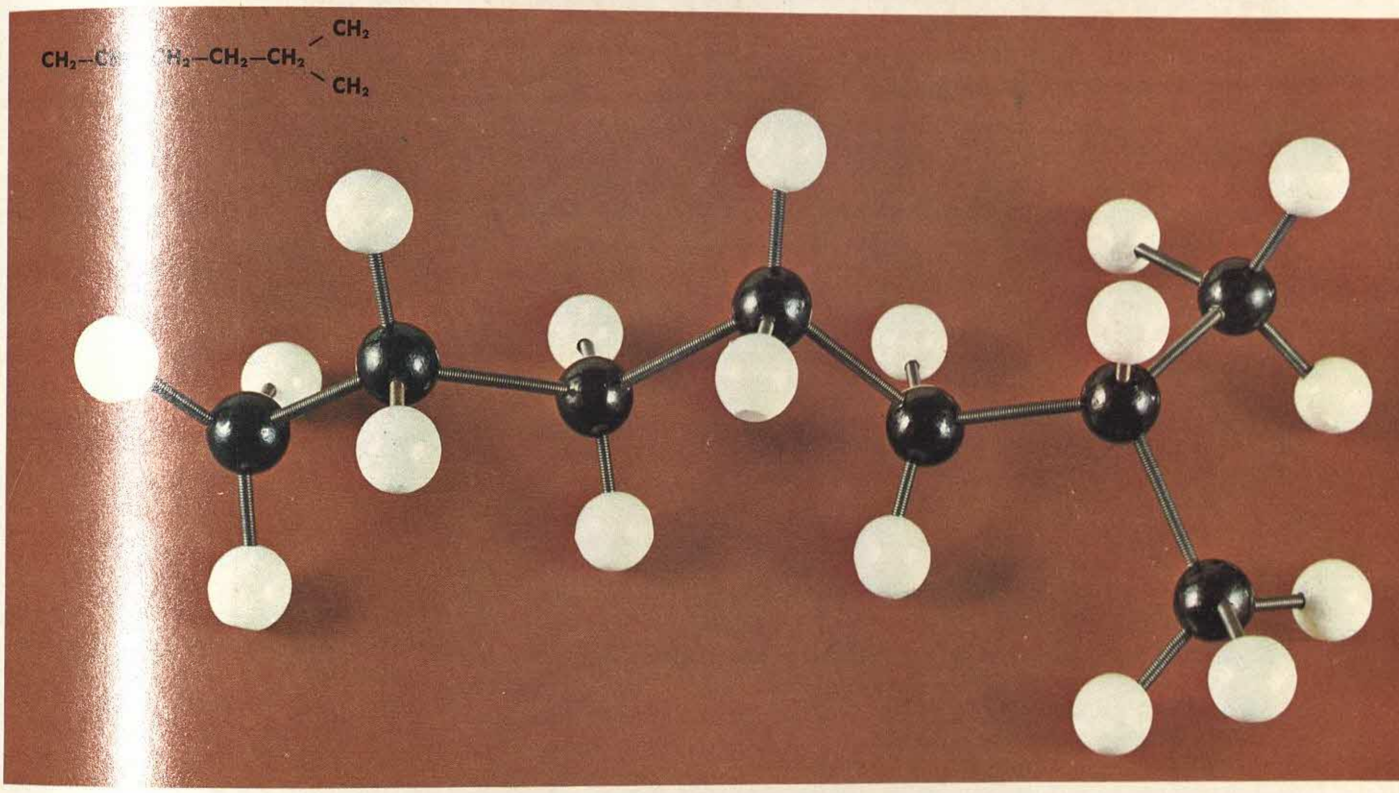
Paraffins were once thought to have an extremely low chemical reactivity. It is true that straight-chain paraffin molecules are resistant to attack by chemical reagents. Despite this low chemical re-

4

REFINING—Petroleum, which is nothing more or less than a mixture of hydrocarbons, is broken down and refined in reaction towers such as this.

NOMENCLATURE—Using IUPAC (International Union of Pure and Applied Chemistry) nomenclature, this compound is called 2-methyl heptane because the side methyl ($-CH_3$) group is attached to the second from the right carbon atom of the seven-carbon-atom chain. The compound could as well be called isooctane; this name, however, is now used for a slightly different hydrocarbon: 2,2,4-trimethyl pentane. This substance is an excellent gasoline, and is one of the standards for the concept of gasoline octane rating.

5



activity, however, there are many ways of making paraffin hydrocarbons react. Those reactions that do take place depend on certain structural peculiarities that appear at high temperatures or in the presence of appropriate catalysts. For example, it has been observed that chlorine and bromine replace the hydrogen atoms in paraffins at ordinary temperatures and in the presence of ultraviolet light; this is a photochemical reaction. In the case of the chlorination of methane, the reaction may take place with explosive violence under certain conditions. This reaction leads to the formation of methyl chloride and higher substitution products:

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$$

methyl chloride

$$CH_3Cl + Cl_2 \rightarrow CH_2Cl_2 + HCl$$

dichloromethane

$$CH_2Cl_2 + Cl_2 \rightarrow CHCl_3 + HCl$$

trichloromethane

$$CHCl_3 + Cl_2 \rightarrow CCl_4 + HCl$$

tetrachloromethane

Tetrachloromethane is also called carbon tetrachloride.

A particularly important industrial reaction of paraffin hydrocarbons occurs when the vapor of a high molecular weight hydrocarbon is passed through a heated pipe at 500 to 700° C (932 to 1,292° F). The reaction that takes place is thermal decomposition, or "cracking." In this reaction the carbon-to-carbon bonds of large molecules are broken into two or more smaller molecular fragments. The net result is a variety of hydrocarbons with fewer carbon atoms, together with gaseous hydrogen and pure carbon in the form of graphite.

Despite the fact that cracking is a complex reaction and produces a variety of products, modern technology depends upon it to produce high-quality gasolines as well as gaseous fuels. Some of these gaseous fuels, propane and butane, for example, are easy to liquefy. They are stored in cylinders under pressure and used as domestic fuels.

The reaction of hydrocarbons with oxygen at high temperatures is very important. This total oxidation, or combustion, liberates large amounts of thermal energy, and is the basis of the use of gasoline in internal combustion engines.

The partial oxidation in air of petroleum paraffins and of high boiling point mineral oils leads to mixtures of higher organic acids similar to those derived from fats. These acids are thus called fatty acids; they are used in soap manufacture. Another very important industrial process is the production of nitroparaffins. These compounds are obtained from saturated hydrocarbons by reaction in the vapor phase with nitric acid at 350 to 500° C (662 to 932° F).

Gaseous hydrocarbons are widespread in nature. Thus, their production by synthesis is usually of little industrial interest. When Germany was isolated from its natural sources of supply during World War II, however, synthetic gasoline was, in fact, produced by means of the Fischer-Tropsch process, which employs the reaction between carbon monoxide (CO) and hydrogen in the presence of special catalysts. The process is feasible because water gas (a mixture of CO and H_2) is easily obtained by passing water vapor over burning coal. The reaction is as follows: $C + H_2O \rightarrow CO + H_2$.

FUNCTIONAL GROUPS | poisons or colorants depending on position

One of the best ways to approach organic chemistry is through the study of functional groups, for the reason that most organic compounds fit into a rational system according to their reactions. It is logical, as well as convenient, to divide organic compounds into families with similar properties, just as the classification in Mendeleev's periodic system lists the elements in groups with analogous, or similar, properties. The chemical properties of any given organic compound (its reaction toward given reagents) generally depend on specific atoms, or groups of atoms, present in the molecule and not on the molecule as a whole.

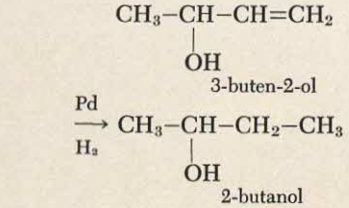
For example, a piece of potassium placed in a container of n-propyl alcohol will produce hydrogen:

$$\underset{\text{n-propyl alcohol}}{2CH_3{-}CH_2{-}CH_2{-}OH + 2K}$$

$$\rightarrow \underset{\text{potassium n-propylate}}{2CH_3{-}CH_2{-}CH_2{-}OK + H_2}$$

The entire molecule of propyl alcohol is not affected by the reaction, which involves substituting potassium for the hydrogen atom of the hydroxyl. The carbon and hydrogen atoms directly attached to them are not involved in this process.

The alcohol 3-buten-2-ol is a compound in which four carbon atoms are arranged in a linear chain having a hydroxyl attached to the second carbon atom and a double bond between the third and fourth atoms. If this unsaturated alcohol were hydrogenated with finely divided palladium as the catalyst, the result would be:



$$CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH{=}CH_2$$

3-buten-2-ol

$$\xrightarrow[H_2]{Pd} CH_3{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_2{-}CH_3$$

2-butanol

This reaction involves only the saturation of the double bond. The hydroxyl $-OH$ is left unchanged. If, on the other hand, the compound were treated with metallic potassium, the hydrogen of the hydroxyl group would be substituted but the double bond would remain intact. These two different reactions demonstrate that the molecule of 3-buten-2-ol contains at least two reaction points: the double bond, in which the molecule reacts like an ordinary alkene, and the hydroxyl group, which reacts like an ordinary alcohol. It is apparent, then, that this group belongs to two distinct classes of organic compounds.

In general, an organic molecule may be considered a combination of a rather nonreactive skeleton (which may be an aliphatic chain or an aromatic or heterocyclic ring) and a functional group–atoms or groups of atoms on which the properties of the molecule depend and that determine the class of organic compounds to which it belongs. The function $-COOH$, for example, is called the carboxyl group, and the compounds which contain it make up the class of carboxylic acids. No functional group can exist in the free state because it contains one or more nonsaturated valences, that is, those that form the bond with the rest of the molecule.

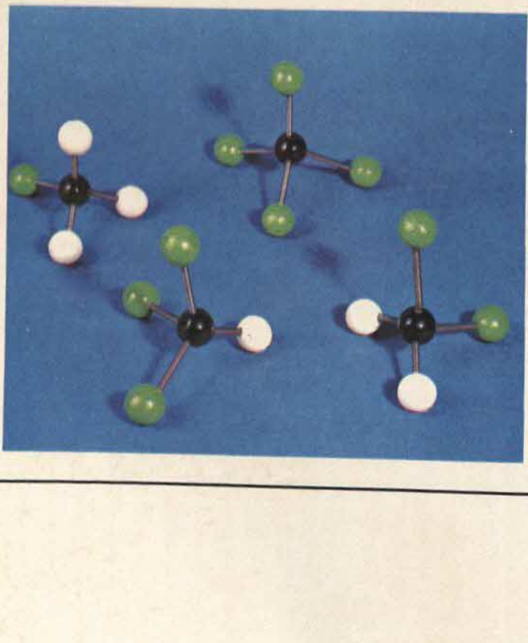
Different functional groups can coexist in the same molecule. As a general rule it can be said that if these functional groups are attached to points widely separated in the molecule, the properties of the molecule itself are simply the sum of the various properties of the single groups. However, if the groups are close to each other, or are actually attached to the same carbon atom, special properties will emerge resulting from interference between the two functions: two hydroxyls, for example, are generally unstable when joined to the same carbon atom.

HALOGEN DERIVATIVES

Organic halogen derivatives are compounds that contain one or more halogen atoms–fluorine, chlorine, bromine, and iodine. Fluorine derivatives have properties that differ from other halogen derivatives. A halogen atom may be introduced into an organic molecule by substitution reaction. In this case, the halogen atom would take the place of an atom or functional group already present. It could also be introduced by unsaturated-bond addition reaction.

ORGANIC HALOGEN DERIVATIVES — These compounds have one or more halogen atoms in their molecules. A halogen atom can be introduced into an organic molecule by substitution reaction (replacing a hydrogen atom or another functional group) or by unsaturated-bond addition reaction. A typical example of a substitution reaction is the direct chlorination of methane. With this reaction four different chlorides are derived that differ only in the number of chlorine atoms they contain. These compounds are chloromethane or methyl chloride (when only one hydrogen atom is replaced with chlorine), dichloromethane (with two chlorine atoms), trichloromethane or chloroform (with three chlorine atoms), and tetrachloromethane or carbon tetrachloride (with four chlorine atoms). In Illustration 1 the green balls are chlorine, the black balls carbon, and the white balls hydrogen.

1



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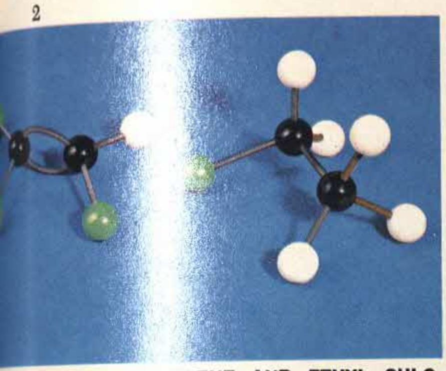
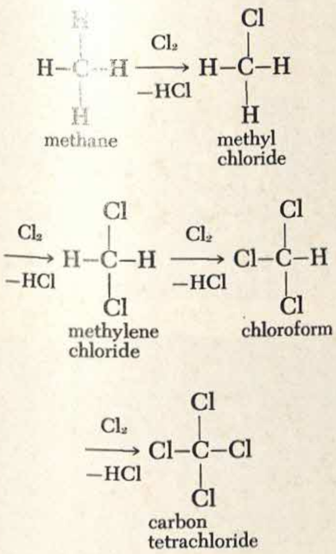


TRICHLOROETHYLENE AND ETHYL CHLORIDE—One of the most widely used solvents for fatty substances is trichloroethylene (on the left). If inhaled at length, its vapors are poisonous. Ethyl chloride (on the right) has only one chlorine atom in its molecule; its chief use is as a local anesthetic because it causes temporary loss of sensitivity to pain when it evaporates.

One example of a substitution reaction is the direct chlorination of methane. This can be achieved either by heating a mixture of chlorine and methane or by irradiating it with ultraviolet light. The first step in the reaction is the substitution of a chlorine atom for one of the methane's hydrogen atoms: the second hydrogen atom is substituted, then the third and finally the fourth:



$$\underset{\text{methane}}{\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}H}} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}} \underset{\text{methyl chloride}}{\mathrm{H{-}\overset{Cl}{\underset{H}{C}}{-}H}}$$

$$\xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}} \underset{\text{methylene chloride}}{\mathrm{H{-}\overset{Cl}{\underset{Cl}{C}}{-}H}} \xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}} \underset{\text{chloroform}}{\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}H}}$$

$$\xrightarrow[-\mathrm{HCl}]{\mathrm{Cl_2}} \underset{\text{carbon tetrachloride}}{\mathrm{Cl{-}\overset{Cl}{\underset{Cl}{C}}{-}Cl}}$$

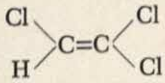
Methane can, therefore, produce four different chloride compounds, which differ in the number of chlorine atoms present in the molecule. In organic compounds an increase in the molecular weight in compounds belonging to the same family usually results in an increase in the boiling and melting points. Methane is a representative example of this phenomenon because the chlorine atom which replaces the hydrogen atom is thirty-five times heavier.

The first substitution produces chloromethane, CH_3Cl, also known as methyl chloride. At room temperature it is a gas, with a boiling point of 24° C (75.2° F). Dichloromethane, or methylene chloride, CH_2Cl_2, is a liquid which boils at a little above room temperature; its boiling point is 40° C (104° F).

The third substitution produces chloroform, $CHCl_3$, a heavy colorless liquid having a characteristically sweetish smell and a boiling point of 61° C (141.8° F). Chloroform was once primarily used as an inhalant anesthetic, but is no longer acceptable for this purpose because of its harmful side effects. However, it is widely used as an efficient solvent for fats and other fairly complicated organic compounds.

Carbon tetrachloride, or tetrachloromethane, CCl_4, is also a heavy colorless liquid with a marked sweetish smell; its boiling point is 77° C (170.6° F). Nonflammable, carbon tetrachloride is especially effective in fire extinguishers; it volatilizes easily and its heavy vapors suffocate flames by cutting off the oxygen supply.

Carbon tetrachloride is a good solvent for fatty substances, and it is therefore important in the manufacture of dry-cleaning products. Other chlorine derivatives are also used in dry-cleaning processes, among which trichloroethylene



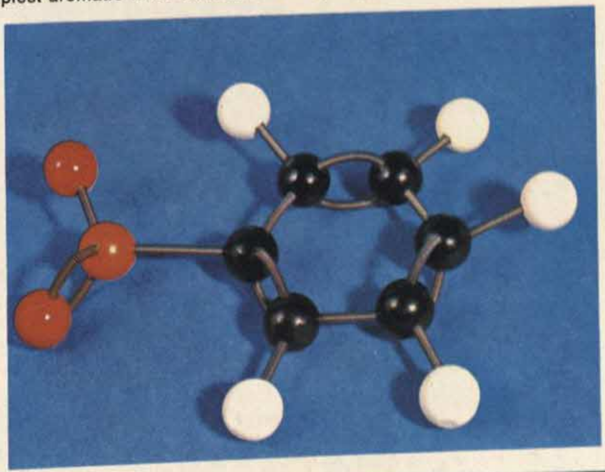
is the most widely used. This derivative must be used with great caution, for prolonged inhalation of its vapors can be extremely dangerous.

Ethyl chloride, $CH_3\text{-}CH_2Cl$, boils at 13° C (55.4° F). A drop of ethyl chloride deposited on the skin will evaporate immediately, but it also freezes the area with which it comes in contact, creating a temporary loss of sensitivity to pain. Because of this, ethyl chloride is often used as a local anesthetic in minor surgery.

Aromatic halogen derivatives are compounds in which a halogen atom is directly attached to a carbon atom that is part of an aromatic ring. These derivatives can only be produced by a substitution reaction. An addition reaction would cause the unsaturation of the aromatic ring to disappear because it would also involve the double bonds. They are stable, rather unreactive compounds in contrast to aliphatic halogen derivatives, which have high reactivity and are important in many organic syntheses.

NITROBENZENE—The molecules of organic nitro derivatives contain an NO_2 group—the nitro group—directly attached to a carbon atom. The simplest aromatic nitro derivative is nitrobenzene. In Illustration 3 the orange ball is the nitrogen, the red balls the oxygen, the black balls the carbon, and the white balls the hydrogen.

3



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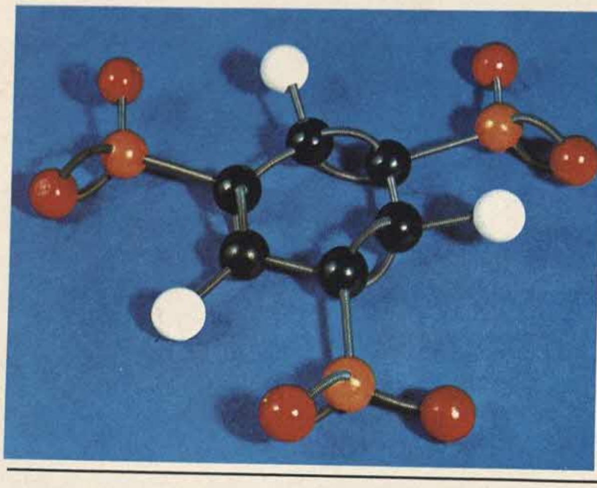
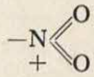


TRINITROBENZENE — A triple-substituted derivative of benzene, trinitrobenzene is an explosive with a high disruptive power, higher in fact than trinitrotoluene (TNT), though less used because of manufacturing difficulties.

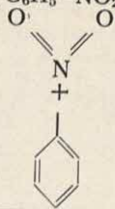
NITRO DERIVATIVES

Organic nitro derivatives are compounds in which a nitro group

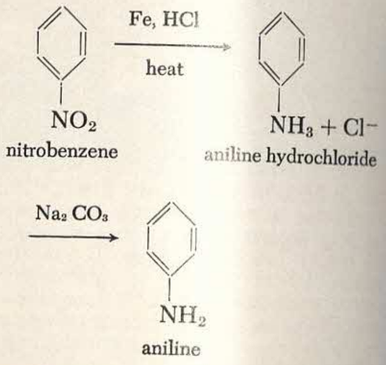


$$-\underset{+}{\mathrm{N}}\genfrac{}{}{0pt}{}{\diagup\mathrm{O}}{\diagdown\mathrm{O}}$$

is directly attached to a carbon atom. One of the aromatic nitro derivatives is nitrobenzene, $C_6H_5-NO_2$:

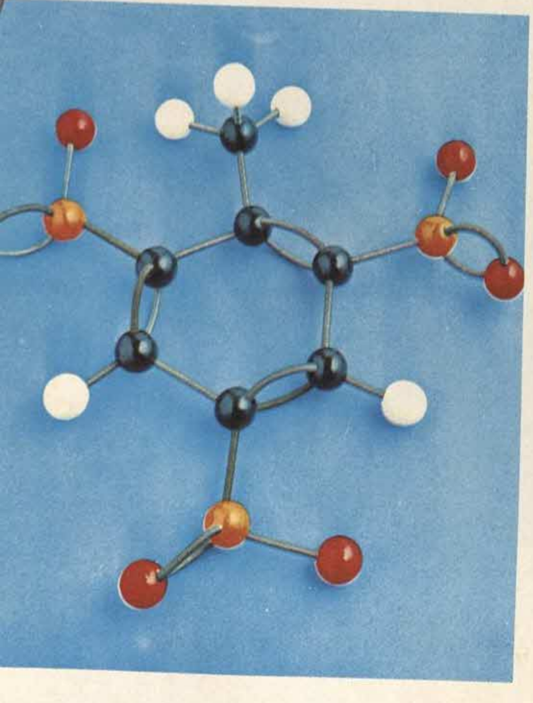


which is formed by treating benzene with a mixture of concentrated nitric and sulfuric acids. Nitrobenzene is commercially important, particularly in the manufacture of aniline, which is a major compound:



5b

5a

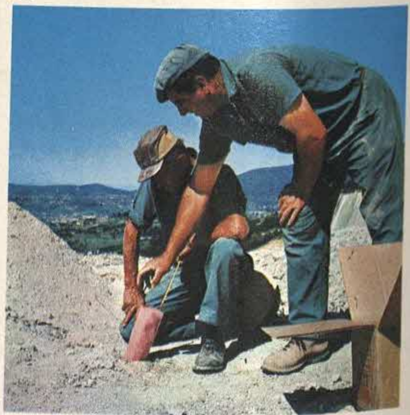


TRINITROTOLUENE—Another important triple-substituted aromatic derivative is trinitrotoluene. Illustration 5a shows its structure.

This important explosive, commonly known as TNT, is manufactured by nitrating toluene with a mixture of sulfuric acid and nitric acid. The process is relatively easy and the yield is high (about 80 percent) because of the activating action of the methyl group ($-CH_3$). TNT is the explosive most widely used to fill grenades and bombs; it can be exploded either by shock or with a detonator such as a capsule of mercury fulminate or lead azide. When the detonator explodes, a powerful wave sets off the TNT.

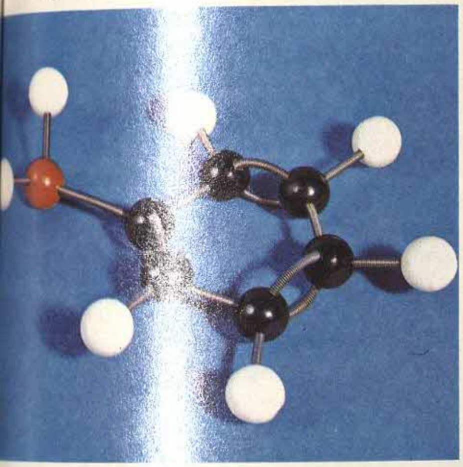
Illustration 5c shows two men preparing a charge of TNT, and Illustration 5b an enormous explosion caused by TNT's high disruptive power.

5c



ANILINE—This compound, which is of enormous importance in industry because of the wide range of products based on it, is obtained by reducing nitrobenzene. Pure aniline is a colorless oil, but when exposed to the air it turns reddish-brown.

6

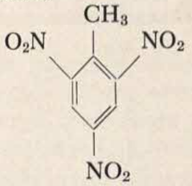


7

PIGMENTS WITH NITRO DERIVATIVE BASES—Aromatic nitro derivatives can cause characteristic reactions important for production in the field of paints and lacquers. The photograph shows three different nitro derivatives characterized by their bright colors.

Nitrobenzene is often used in cheap perfumes because of its delicate smell, somewhat similar to that of bitter almonds.

Trinitrotoluene,



better known as TNT, is a commonly used explosive and is the chief reason for the industrial importance of toluene. During World War II, the normal source of toluene was coal tar, but it provided an insufficient supply. Industry had to turn to new methods for obtaining toluene from gasoline.

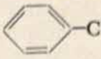
Nitromethane, CH_3-NO_2, is an example of a paraffin nitro derivative. Nitro derivatives can easily be reduced to amines:

$$R-NO_2 + 3H_2 \longrightarrow R-NH_2 + 2H_2O.$$

This reaction is employed chiefly for aromatic amines, which are of primary importance in industry as basic ingredients in colorants, drugs, and so forth. Industry favors these aromatic nitro derivatives because they are fairly easy to manufacture by reaction with a mixture of sulfuric and nitric acids.

Nitroparaffins are classified as primary, secondary, or tertiary. Primary nitroparaffins have two (or three) hydrogen atoms attached to the carbon holding the nitro group; for example, 1-nitropropane, nitromethane, and nitroethane, $CH_3CH_2NO_2$. Secondary nitroparaffins have but one hydrogen atom on the carbon holding the nitro group, for example, 2-nitropropane, while tertiary nitroparaffins have no hydrogen atoms attached to the carbon holding the nitro group, for example, 2-methyl-2-nitropropane. Tertiary nitroparaffins do not react with bases and, hence, they fail to exhibit many of the common reactions of primary and secondary nitroparaffins.

CLASSIFICATION OF ORGANIC COMPOUNDS ACCORDING TO THEIR FUNCTIONAL GROUPS

Class	Functional Group	Example	
		Formula	Name
alkene	$>C=C<$	$CH_3-CH=CH_2$	propylene
alkyne	$-C\equiv C-$	$CH_3-C\equiv CH$	methylacetylene
alcohol	$-OH$	$CH_3-CH_2-CH_2-OH$	n-propanol
ether	$-O-$	$CH_3-O-CH_2-CH_3$	methyl ethyl ether
halide	$-F$, $-Cl$, $-Br$, $-J$	CH_3-CH_2-Br	bromoethane
nitro derivative	$-NO_2$	$CH_3-CH_2-NO_2$	nitroethane
carboxyl acid	$-COOH$	CH_3-CH_2-COOH	propionic acid
aldehyde	$-CHO$	CH_3-CH_2-CHO	propionaldehyde
ketone	$-CO-$	$CH_3-CO-CH_2-CH_3$	methyl ethyl ketone
amine	$-NH_2$	$CH_3-CH_2-NH_2$	ethylamine
organometallic	$-\overset{\vert}{\underset{\vert}{C}}-\text{metal}$	$CH_3-CH_2-CH_2-CH_2-Li$	butyl lithium
sulfonic acid	$-SO_3H$	$CH_3-CH_2-SO_3H$	ethansulfonic acid
nitrile	$-CN$	 $-CN$	benzonitrile
ester	$-COOR$	$CH_3-COOCH_3$	methyl acetate
amide	$-CO-NH_2$	$CH_3-CO-NH_2$	acetamide

ORGANIC REACTIONS | addition mechanisms

Numerous examples of organic reactions have been discussed in previous articles. The majority of these reactions are included in four fundamental types—addition, substitution, elimination, and transposition.

Before considering these four types, however, it is desirable to recall how organic reagents are classified. Polar reagents, either organic or inorganic, are subdivided into two basic groups: electrophilic and nucleophilic. Electrophilic reagents tend to acquire electrons. Such reagents will preferentially attack carbon atoms that have a great amount of free electron density; their behavior resembles that of cations (positive ions). In a previous article various reactions were discussed involving aromatic nuclei that are attacked by electrophilic substances.

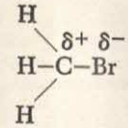
The most common electrophilic reagents are:

HNO_3, H_2SO_4, HNO_2, H^+, BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_3$, Br_2, Cl_2, $>C{=}O$, and CO_2.

Nucleophilic reagents, on the other hand, tend to give up electrons and will, therefore, attack sites on organic molecules that are electron-deficient; their behavior resembles that of anions (negative ions). Typical nucleophilic reagents are:

Cl^-, Br^-, HO^-, RO^-,
RS^-, CN^-, $R{-}C{\equiv}C^-$,
$>O$ (ethers), $\Rrightarrow N$ (amines), $>S$ (thioethers)
$R{-}MgBr$, $R{-}M$
(where M represents an alkaline metal).

A carbon atom susceptible to attack by a nucleophilic reagent is the carbon atom of methyl bromide:



This atom is electron deficient because of the greater electronegativity of the halogen (Br).

According to the Lewis acid-base theory, electrophilic substances such as aluminum chloride ($AlCl_3$) are considered acids. Nucleophilic substances such as the tertiary amines (R_3N), on the other hand, are considered bases.

Thus, the reaction mechanisms of polar reagents clearly indicate the importance of electron distribution in organic reactions. In other cases, the reactive spe-

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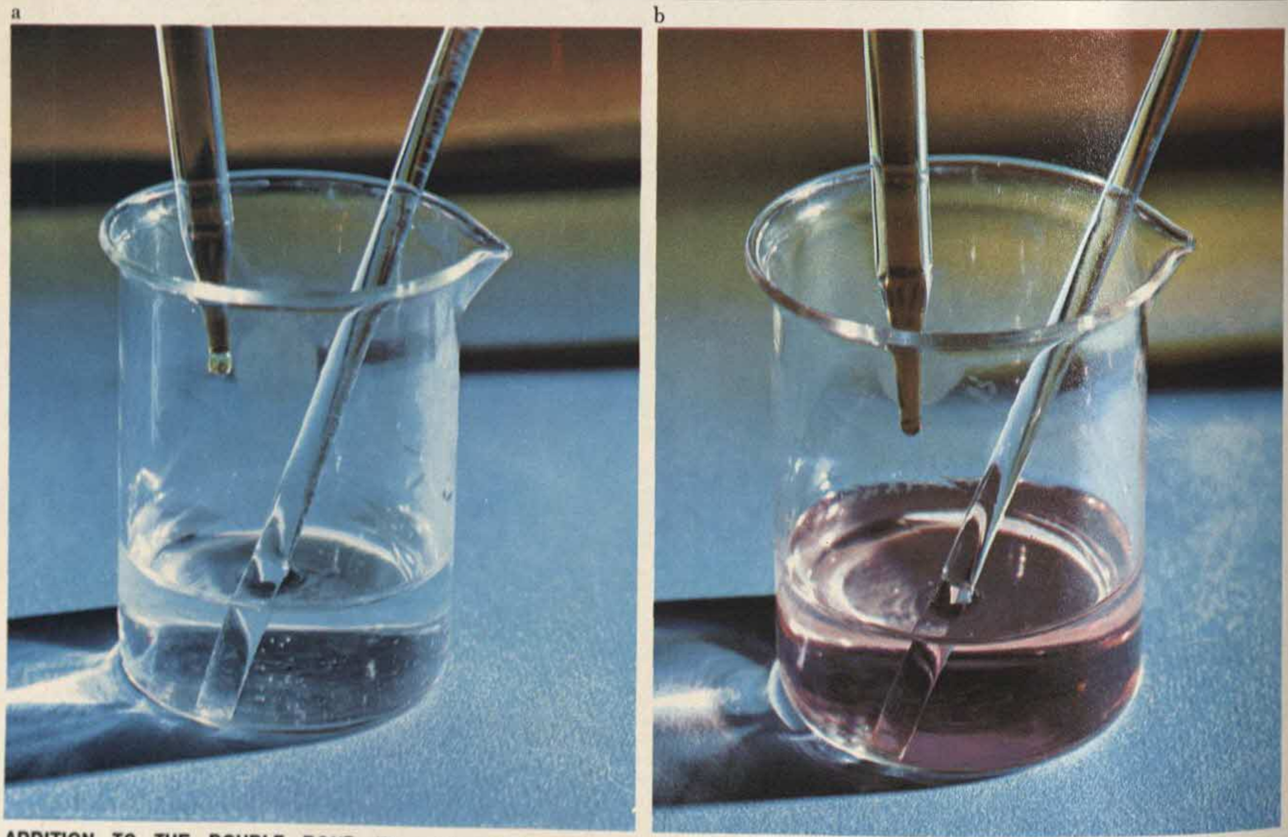


ADDITION TO THE DOUBLE BOND—The double bond, by virtue of its high electron density, is readily attacked by electrophilic reagents (halogens, acids, and oxidizing agents). This type of reaction finds use in analyzing for the presence of the double bond. Thus, iodine bromide is now an important analytical reagent because it adds to a π bond even more easily than does bromine; it also offers other advantages, including the fact that it can be titrated with thiosulfate. In this respect it behaves like iodine, but is far more reactive. Illustration 1a shows a solution of iodine bromide in acetic acid with the solution nearing the titration end point with n-octene.

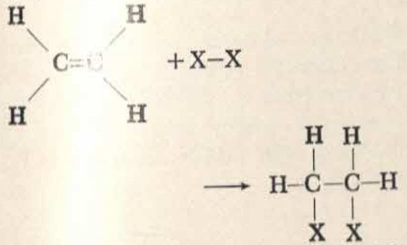
In Illustration 1b this titration has been completed. Excess iodine bromide will be decomposed by means of starch water and the liberated iodine will be titrated with thiosulfate. The moles of octene will then be obtained by difference. Iodine bromide is used also to analyze the double bond in particularly difficult cases; for example, when the degree of unsaturation of a polymer prior to vulcanization is desired.

cies behave as free radicals rather than negative or positive ions. In these cases electron distribution in the organic molecule is no longer of paramount importance.

In general, therefore, organic reactions will be described as electrophilic, nucleophilic, or free radical in terms of whether the reaction is begun by an electrophilic, nucleophilic, or free radical reagent.

ADDITION

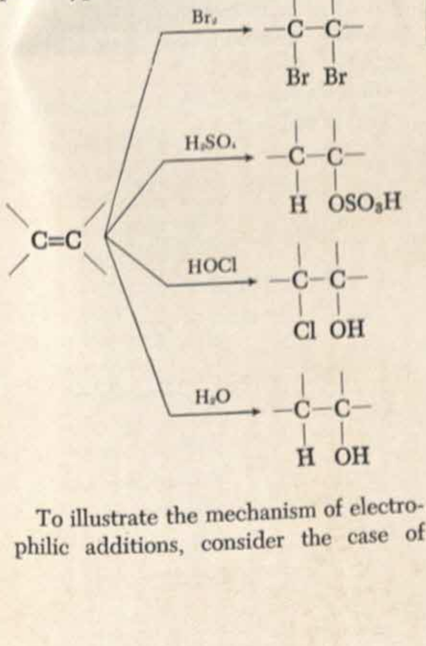
The most common and important addition reactions involve the double bonds >C=C< and >C=O. Addition to the double bond >C=C<



can occur via either an electrophilic mechanism or a free radical mechanism.

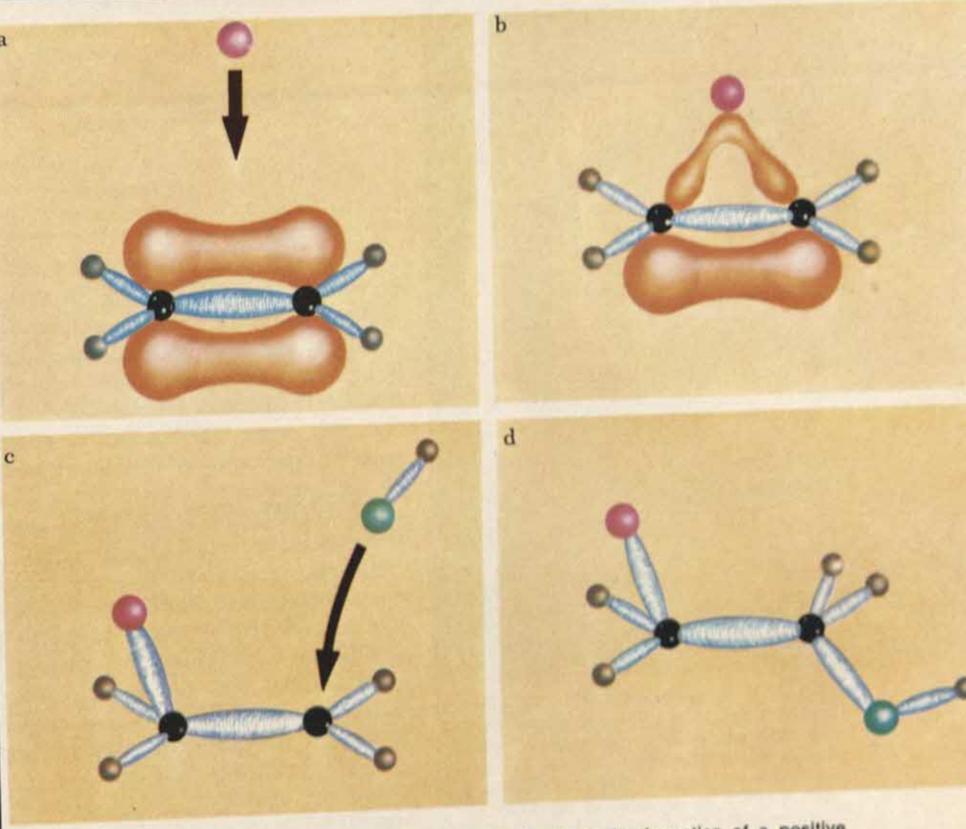
Addition reactions of the electrophilic type occur more readily in polar solvents (water, alcohol, and so forth), while free radical reactions take place more readily in nonpolar solvents. All reactions involving free radicals, moreover, are facilitated by the presence of free radicals and by the action of radiation.

Many of the addition reactions previously encountered are of the electrophilic type.



To illustrate the mechanism of electrophilic additions, consider the case of

2



THE MECHANISM OF ADDITION TO π BONDS—These four illustrations show schematically the mechanism of addition to the double bond.

Illustration 2a shows the ethylene molecule's π orbital. This is the point of attack for electrophilic reagents, as well as for the approaching cation Br^+. The result (Illustration 2b) is formation of a complex compound from the bromine and the π orbital. This compound is known as the π complex.

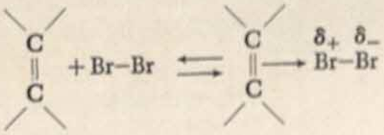
The approach of a negative ion (Illustration 2c) causes this complex compound to break up. This leads to the formation of a positive complex ion.

The principal anions present in an aqueous solution will be hydroxide ions. The positive complex ion will, therefore, react with the hydroxide ions rather than with the rarer bromide ions Br^-.

The presence of bromine, however, prevents addition of the hydroxyl in the *cis* position. The ultimate product will thus have the *trans* structure shown schematically in Illustration 2d.

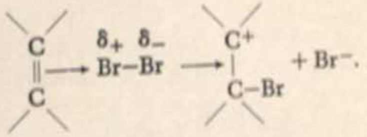
bromine. It is thought that the addition process takes place in the following steps:

1. Interaction of the bromine with the electrons of the double bond

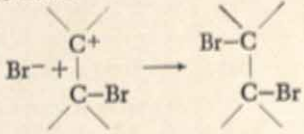


leading to the formation of a complex that cannot be isolated, and in which the Br_2 molecule is polarized with the positive end facing the double bond.

2. Breakage of the bond between the bromine atoms and formation of a positive ion and a bromide ion



3. Attack of the bromide ion, preferentially *trans* to (on the sides opposite to) the originally formed carbon-bromine bond.



The stereochemical development of halogen addition is obvious in the case

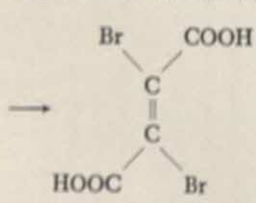
3

ADDITION TO THE CARBONYL GROUP—The carbonyl double bond is also subject to addition reactions. In this case, however, polarization of the bond ensures that the carbon will be positively charged. It is consequently subject to attack by nucleophilic reagents.

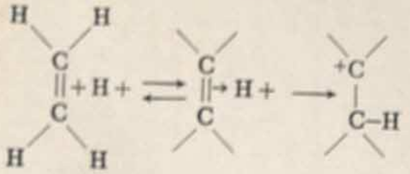
The compound shown is the result of addition of sodium bisulfite to an aldehyde. The nucleophilic reagent in this particular case is SO_3H^-.

of acetylene compounds. In this case the reaction product contains a double bond; the result is the *trans* isomer.

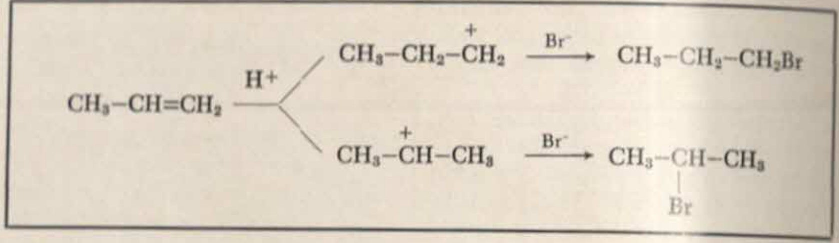
$$HOOC{-}C{\equiv}C{-}COOH + Br_2$$



An analogous mechanism is thought to be involved in other electrophilic addition reactions. For example,



When the olefin is unsymmetrical, two orientations are possible:



The second product is usually formed because of the greater tendency of the positive charge to become localized on secondary carbon atoms. This orientation is expressed by Markovnikov's rule: In addition reactions to unsymmetrical olefins, the more electronegative group tends to react with the most substituted of the unsaturated carbon atoms (in $CH_3CH{=}CH_2$, this is the carbon atom that carries the methyl group, $-CH_3$).

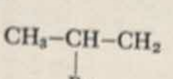
The other possible addition reaction to the carbon-carbon double bond is the free radical type. A typical example is addition of a halogen acid to an unsymmetrical olefin, with the reaction taking place in the presence of small quantities of organic peroxides (RO−OR′). Such peroxides are easily split into free radicals (RO· and R′O·), which are then capable of generating new free radicals from the reagents present. A rapid chain reaction results with the addition orientation opposite to that of the electrophilic addition discussed previously.

$$RO\cdot + HBr \longrightarrow ROH + Br\cdot$$

$$CH_3{-}CH{=}CH_2 + Br\cdot \longrightarrow CH_3{-}\dot{C}H{-}CH_2Br$$

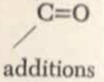
$$CH_3{-}\dot{C}H{-}CH_2Br + HBr \longrightarrow CH_3{-}CH_2{-}CH_2Br + Br\cdot$$

The bromine free radical formed during the third step then attacks another propylene molecule. The reason for the formation of $CH_3{-}CH_2{-}CH_2Br$ lies in the greater stability of the secondary radical $CH_3{-}\dot{C}H{-}CH_2Br$ compared to the primary radical

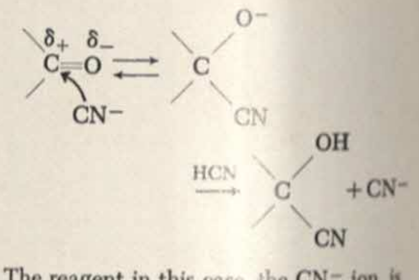


$$CH_3{-}\underset{\displaystyle Br}{\underset{|}{C}H}{-}\dot{C}H_2$$

Addition to the double bond >C=O is of a polar character; unlike what happens in the case of the double bond >C=C<, this reaction is generally nucleophilic. The mechanism derives from the degree of polarization of the carbonyl group, which is due to the greater electronegativity of oxygen:



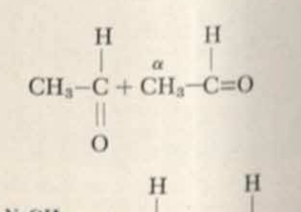
Numerous additions of this type have been discussed in the aldehyde and the ketone articles. As an example, recall the reaction of carbonyl compounds and hydrocyanic acid (HCN, ionized into H⁺ and CN⁻):



The reagent in this case, the CN⁻ ion, is obviously nucleophilic in character.

When acetaldehyde is treated with a small quantity of sodium hydroxide, it forms aldol; this reaction may be regarded as involving the addition of one molecule of acetaldehyde to the carbonyl group of another.

The structure of this reaction may be stated as follows:



aldol

ABBREVIATIONS

A	ampere
Å	Angstrom unit
abs	absolute
a-c	alternating current (as an adjective)
amu	atomic mass unit
atm	atmosphere
at. wt	atomic weight
AU	astronomical unit
avdp	avoirdupois
Bev	one billion electron volts
bhp	brake horsepower
bhp-hr	brake horsepower-hour
bp	boiling point
Btu	British thermal unit
C	temperature Celsius; temperature Centigrade
c	candle
cal	calorie
cfm	cubic feet per minute
cfs	cubic feet per second
cgs	centimeter-gram-second (system)
cl	centiliter
cm	centimeter
cm^2	square centimeter
cm^3	cubic centimeter
coef	coefficient
colog	cologarithm
cos	cosine
cot	cotangent
cp	candlepower
csc	cosecant
cu	cubic
cu ft	cubic foot
db	decibel
d-c	direct current (as an adjective)
doz	dozen
E	electromotive force
e	the base of the system of natural logarithms
ev	electron volt
F	temperature Fahrenheit
fp	freezing point
fpm	feet per minute
fps	feet per second
ft	foot; feet
ft^2	square foot
ft^3	cubic foot
ft-c	footcandle
ft-lb	foot-pound
G	universal gravitational constant
g	gram
gal	gallon
g-cal	gram-calorie
gpm	gallons per minute
gps	gallons per second
hr	hour
hν	photon energy
hp	horsepower
Hz	hertz (cycles per second)
I	electric current
ID	inside diameter
in.	inch
in.^{2}	square inch
in.^{3}	cubic inch
in.-lb	inch-pound
ips	inches per second
j	joule
K	temperature Kelvin (absolute)
kcal	kilocalorie
kg	kilogram
kg-cal	kilogram-calorie
kg-m	kilogram-meter
kg/m^3	kilograms per cubic meter
kgps	kilograms per second
km	kilometer
kv	kilovolt
kw	kilowatt
kwhr	kilowatt-hour
l	liter; lumen
lat	latitude
lb	pound
lb-ft	pound-foot
lb/ft^2	pounds per square foot
lb/ft^3	pounds per cubic foot
lb-in.	pound-inch
l-hr	lumen-hour
lin ft	linear foot
log	logarithm (common)
log$_e$	logarithm (natural)
long.	longitude
m	meter; minute (time, in astronomical circles)
m^2	square meter
m^3	cubic meter
ma	milliampere
Mev	one million electron volts
mg	milligram
mh	millihenry
mi	mile
mi^2	square mile
min	minute
m-kg	meter-kilogram
ml	milliliter
mm	millimeter
mm^2	square millimeter
mm^3	cubic millimeter
mμ	millimicron
mph	miles per hour
mphps	miles per hour per second
mv	millivolt
N	Avogadro's constant
n!	factorial *n*
OD	outside diameter
oz	ounce
pH	rating on acid-alkaline scale
ppm	parts per million
psi	pounds per square inch
psia	pounds per square inch absolute
R	temperature Reaumur; resistance
RA	right ascension
rpm	revolutions per minute
rps	revolutions per second
sec	secant; second
sin	sine
sp gr	specific gravity
sq	square
tan	tangent
V	volt
VA	volt-ampere
W	watt; work
yd	yard
yd^2	square yard
yd^3	cubic yard

SCIENTIFIC SYMBOLS AND ABBREVIATIONS

α	alpha particle
β; β^-	beta particle
β^+	positron
γ	gamma radiation
Δ	a small change; heat
λ	wavelength; radioactive-decay constant
ma	milliampere
μc	microcurie
μf	microfarad
μin.	microinch
μm	micron
$\mu\mu$	micromicron
$\mu\mu$f	micromicrofarad
ν	frequency; neutrino
π	3.14159; osmotic pressure
Σ	the sum of
σ	nuclear cross section (barns); area
Ω	electrical resistance (ohms)
ω	angular speed; angular velocity
′	minute (angular measure)
″	second (angular measure)
♂	male
♀	female
$>$	is greater than
$<$	is less than
$\propto$	is proportional to
∞	infinity
$\sqrt{\ }$	square root of
°	degrees; temperature; angle measurement (example, 30°)
[ ]	molar concentration
+	positive electric charge; mixed with; plus
−	negative electric charge; single covalent bond; minus
=	equals; double covalent bond; produces
≠	does not equal
≡	triple covalent bond
→	produces; forms; chemical reaction
⇄	reversible chemical reaction
↑	gas produced by a chemical reaction
↓	precipitate produced by a chemical reaction
*	radioactive substance (follows symbol of element; example, Cl^*)

THE
ILLUSTRATED SCIENCE
DICTIONARY

Laws of Science to Mesoderm

KEY TO PRONUNCIATION

The diacritical marks are:

ə	b*a*nan*a*, *a*but	e	b*e*t	th	*th*in
ᵊ	preceding l, m, n as in batt*le*	ē	b*ea*t	t̲h̲	*th*en
ə̇	*e*lectric	i	t*i*p	ü	r*u*le, f*oo*l
ər	f*ur*ther	ī	b*i*te	u̇	p*u*ll, w*oo*d
a	m*a*t	j	*j*ob, *g*em	ue	German h*ü*bsch
ā	d*ay*	ŋ	si*ng*	u̅e̅	French r*ue*
ä	c*o*t, f*a*ther	ō	b*o*ne	yü	*u*nion
au̇	n*ow*, *ou*t	ȯ	s*aw*, *a*ll	zh	vi*si*on
		ȯi	c*oi*n		

ˈ mark preceding the syllable with strongest stress.
ˌ mark preceding a syllable with secondary stress.

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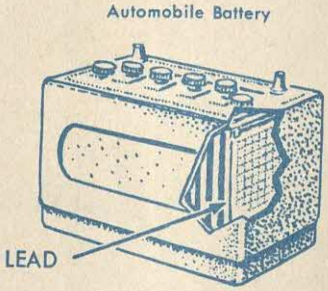
laws of science \\'lȯz əv 'sī-ən(t)s\\
Statements or generalizations about certain orderly relationships among phenomena, based on scientific observation and verification.

Robert Boyle's discovery that the volume of a gas varies inversely with pressure when the temperature is held constant is one of the LAWS OF SCIENCE.



laws of thermodynamics \\'lȯz əv ˌthər-mə-(ˌ)dī-'nam-iks\\
PHYSICS. The three laws basic to that branch of physics dealing with the relationships of heat energy to mechanical and other forms of energy. The laws are (1) energy cannot be created or destroyed, but may be changed from one form to another; (2) heat cannot pass spontaneously from a colder body to a hotter body; (3) a perfect crystalline substance has zero entropy at 0° K. (a temperature impossible to reach).

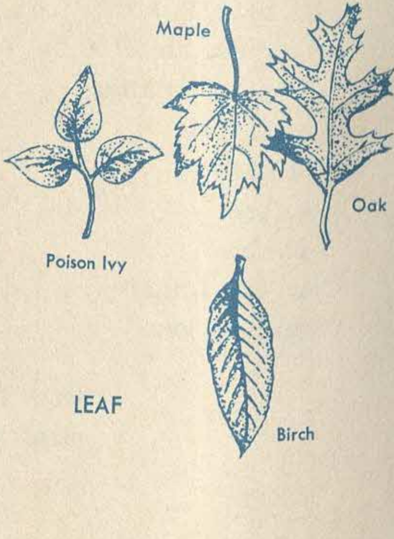
Some physicists accept only the first two LAWS OF THERMODYNAMICS.

leach \\'lēch\\ *v.*
1. CHEMISTRY. To dissolve soluble substances out of a mixture by soaking, or by percolating water or a chemical solution through it. 2. EARTH SCIENCE. To dissolve soluble minerals in soil by water that passes through it.

In the recovery of copper from its ore, sulfuric acid is sometimes used to LEACH *the ore.*

lead \\'led\\ *n.*
CHEMISTRY. A soft, dense metallic element that is relatively resistant to corrosion and has a density of 11.34 grams per cubic centimeter. Symbol, Pb; atomic number, 82; atomic weight, 207.19.

LEAD *is used to form the electrodes in automobile batteries.*



leaf \\'lēf\\ *n.*
1. BOTANY. In plants, an outgrowth from a stem. It manufactures sugar by photosynthesis and usually consists of a flattened, green blade that is joined to the stem by a petiole. 2. PHYSICS. A thin, metallic foil.

The outer covering, or the epidermal cells, of a LEAF *contains the stomata.*

least common denominator \\'lēst 'käm-ən di-'näm-ə-ˌnāt-ər\\
MATHEMATICS. The least common multiple of the denominators of a given set of two or more fractions.

The LEAST COMMON DENOMINATOR *of the fractions* $\frac{1}{3}$, $\frac{5}{6}$ *and* $\frac{5}{8}$

is 24 because it is the least common multiple of the denominators 3, 6 and 8.

LEEWARD

least common multiple \\'lēst 'käm-ən 'məl-tə-pəl\\

MATHEMATICS. The smallest whole number that is evenly divisible by each of a given set of numbers.

The LEAST COMMON MULTIPLE *of 9, 12, 18 and 24 is 72.*

leavening \\'lev-(ə-)niŋ\\ *n.*

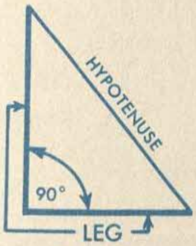
CHEMISTRY. The process of fermentation in unbaked dough that produces carbon dioxide gas. The process causes dough to rise and results in a light, porous product after baking.

Baking powder is added to cake mixes to cause LEAVENING.

Le Chatelier's principle \\ˌlə 'shät-ᵊl-ˌyāz 'prin(t)-s(ə-)pəl\\

CHEMISTRY. A principle that applies to conditions of dynamic equilibrium and states that, if the conditions of a system at equilibrium are changed, the equilibrium will shift in such a direction as to restore the original conditions. Every system in equilibrium, according to the principle, tends to resist changes on it by reacting to nullify the change imposed.

The tendency of one volume of nitrogen mixed with three volumes of hydrogen to form two volumes of ammonia gas when pressure is applied is an excellent illustration of LE CHATELIER'S PRINCIPLE.



(of right triangle)

leeward \\'lē-wərd\\ *adj.*

EARTH SCIENCE. Pertaining to the side or direction opposite to that from which the wind blows; the sheltered side.

The LEEWARD *side of a mountain usually receives less rainfall than the windward side.*

leg \\'leg\\ *n.*

1. MATHEMATICS. In a right triangle, one of the sides adjacent to the right angle. 2. ANATOMY and ZOOLOGY. An appendage used for locomotion.

Either LEG *of a right triangle is shorter than the hypotenuse.*

lens \\'lenz\\ *n.*

1. PHYSICS. A device that will converge or diverge parallel beams of radiation passing through it. It is generally made of a curved piece of glass or plastic to focus the light. 2. ANATOMY. That part of the eye, located just back of the iris, that focuses

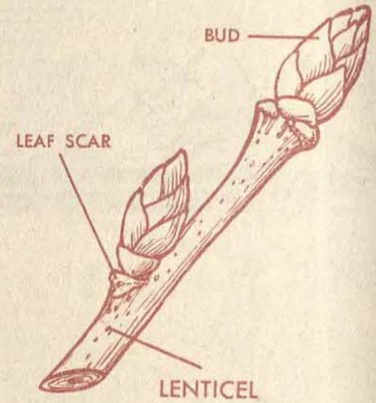
light rays on the retina. 3. EARTH SCIENCE. A rock shaped like a double convex lens.

The LENS *of an optical microscope is glass, but the lens of an electron microscope is a magnetic field.*

lenticel \'lent-ə-ˌsel\ *n.*

BOTANY. A pore in a stem that permits the passage of gas inward and outward.

A LENTICEL *is usually formed just beneath a stoma.*



Lenz's law \'len(t)s-əs 'lȯ\

PHYSICS. The law stating that an induced electric current always has such a direction that its magnetic field opposes whatever action induced it.

According to LENZ'S LAW, *a metal pendulum bob swinging through a magnetic field will be damped by the electric currents induced in it.*

lesion \'lē-zhən\ *n.*

MEDICINE. Any injury or wound; also, a change in any tissue that is due to injury or disease.

A sprain is a LESION *occurring in the ligaments of a joint.*

lethal gene \'lē-thəl 'jēn\

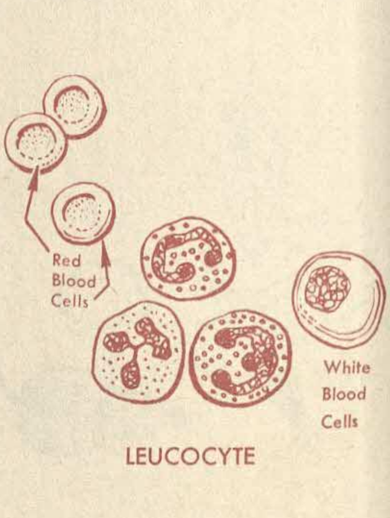
BIOLOGY. Any hereditary factor, or gene, that, when present in both the sperm and egg cells, will cause the death of the organism that develops from their union.

Since a LETHAL GENE *is recessive, its presence in a living individual is masked by a normal gene.*

leucocyte \'lü-kə-ˌsīt\ *n.*

PHYSIOLOGY. A white blood cell, or corpuscle, that is capable of destroying many disease-producing organisms that enter the body.

A LEUCOCYTE *leaves the capillaries and, by squeezing between cells, enters infected tissue.*



LEUCOCYTE

leucoplast \'lü-kə-ˌplast\ *n.*

BOTANY. Colorless bodies, or plastids, found in the cytoplasm of certain plant cells. Leucoplasts often develop into chromoplasts and chloroplasts.

A LEUCOPLAST *serves as the nucleus for the growth of a starch grain.*

lever \'lev-ər\ *n.*

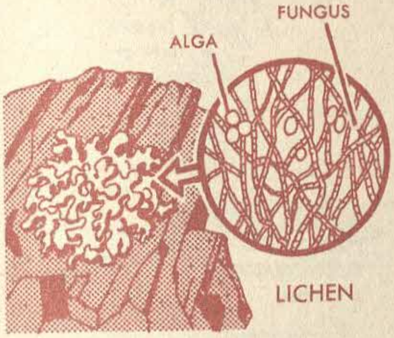
PHYSICS. A rigid bar that is free to turn on a fixed pivot (fulcrum); one of the simple machines that multiplies force.

A hammer used to pull nails acts as a LEVER.

levulose \'lev-yə-ˌlōs\ *n.*

BOTANY and CHEMISTRY. $C_6H_{12}O_6$. A sugar that occurs in honey and many fruits.

One molecule of ordinary table sugar, sucrose, may be broken down into molecules of LEVULOSE *and glucose.*



LICHEN

libration \lī-'brā-shən\ *n.*

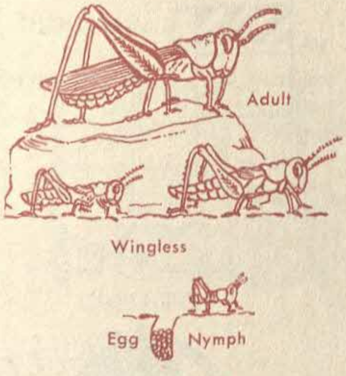
ASTRONOMY. The apparent rocking motions, or oscillations, of the moon as it revolves around the earth. The movements are caused by the inclination of the moon's axis of rotation and the variations in its rate of revolution.

Although the same half of the moon is always turned toward the earth, small areas near the moon's edge appear and disappear from sight from time to time because of the moon's LIBRATION.

lichen \'lī-kən\ *n.*

BOTANY. An unusual plant made up of two organisms, an alga and a fungus, living together in a symbiotic, or mutually dependent relationship. It is of the class Lichenes.

A LICHEN *common in most areas forms a gray-green crusty growth on rocks and tree trunks.*



LIFE CYCLE
GRASSHOPPER

life \'līf\ *n.*

BIOLOGY. A state of matter characterized by certain functional and structural characteristics, such as metabolism, growth, reproduction, sensitivity to stimulation, differentiated cell or tissue development and identifiable individual forms.

All forms of living things come from preexisting LIFE.

life cycle \'līf 'sī-kəl\

BIOLOGY. The series of stages, or changes in form and function, through which a plant or animal passes during one complete generation.

There is alternation of generations in the LIFE CYCLE *of a fern.*

lift \'lift\ *n.*

AERONAUTICS. The upward force on an airplane that is produced by the motion of the air over the wings and, to a much lesser extent, the upward push of air on the bottom of the wings.

The LIFT produced by air flowing over an airfoil is an example of Bernoulli's principle.

ligament \'lig-ə-mənt\ *n.*

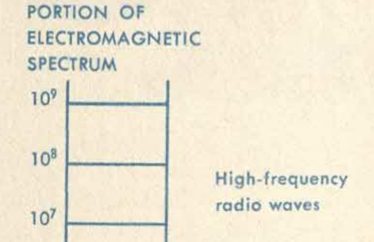
ANATOMY. Strong, tough strands of connective tissue that hold bones together at the movable joints or that hold certain internal organs in place.

A torn LIGAMENT may be a more serious injury than a broken bone.

light \'līt\ *n.*

PHYSICS. Those frequencies of electromagnetic radiation that can be detected by the eye.

The speed of LIGHT in water or in other transparent materials is slower than in a vacuum.



lightning \'līt-niŋ\ *n.*

EARTH SCIENCE. A discharge of static electricity between clouds or between a cloud and the earth's surface.

The electrical charges that produce LIGHTNING are the result of friction between air and water droplets.

light-sensitive \'līt 'sen(t)-sət-iv\ *adj.*

CHEMISTRY. Referring to certain substances that undergo chemical reaction as a result of absorbing light energy.

Ordinary photographic film is made by placing a LIGHT-SENSITIVE silver compound on a celluloid or plastic backing.

light-year \'līt-ˌyi(ə)r\ *n.*

ASTRONOMY. The distance that light travels in one year, or about six trillion miles.

A LIGHT-YEAR is about 63,000 times the distance from the earth to the sun.

ligneous \'lig-nē-əs\ *adj.*

BOTANY. Having the qualities of, or being like, wood; woody.

LIGNEOUS plant stems are more rigid than are the stems of most herbs.

lignin \'lig-nən\ *n.*

BOTANY. A substance that, together with cellulose, forms the woody cell walls of plants and the cementing material between them, thus giving the cells added strength.

LIGNIN *has a higher carbon content than cellulose.*

lignite \'lig-ˌnīt\ *n.*
EARTH SCIENCE. A low-grade soft coal having a woody appearance. It is more compact than peat and less compact than bituminous coal.

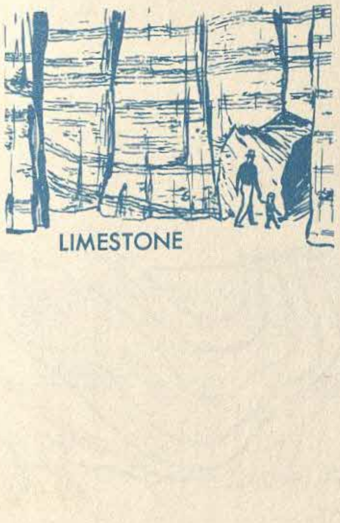
When LIGNITE *is burned, it produces less heat and more smoke than would the same amount of bituminous coal.*

limb \'lim\ *n.*
1. ANATOMY and ZOOLOGY. A jointed part of the body, as a leg or an arm. 2. BOTANY. An offshoot from the main stem of a tree, shrub or flower; a branch. 3. ASTRONOMY. The outer edge of the apparent disks of the sun, moon and planets.

Each flipper of animals such as the sea turtle, seal, walrus and whale is a type of LIMB *adapted to locomotion in water.*

limestone \'līm-ˌstōn\ *n.*
EARTH SCIENCE. A sedimentary rock composed mostly of the mineral calcite, $CaCO_3$, that has been formed by organic or inorganic processes.

Large caves are often formed in deposits of LIMESTONE.



limit \'lim-ət\ *n.*
MATHEMATICS. The number or point toward which a sequence or a series converges; also, the value approached by the dependent variable of a function as the independent variable approaches a given value.

The series $.3 + .03 + .003 + \ldots + 3(10)^{-n} + \ldots$ *has as its* LIMIT *the rational number* $\frac{1}{3}$.

limnetic \lim-'net-ik\ *adj.*
BIOLOGY. Referring to the open part of a body of fresh water, or to something within that zone.

A freshwater lake usually contains hundreds of LIMNETIC *organisms.*

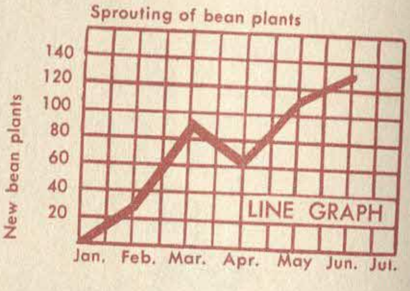
limnology \lim-'näl-ə-jē\ *n.*
The study of the physical, biological, chemical and meteorological conditions in fresh water; particularly, those conditions in ponds and lakes.

The biological aspects of LIMNOLOGY *are called freshwater ecology.*

linear \'lin-ē-ər\ *adj.*

MATHEMATICS. Pertaining to a line; also, having one dimension; also, referring to an equation whose graph is a straight line.

There are three LINEAR *feet in a yard.*



linear equation \'lin-ē-ər i-'kwā-zhən\

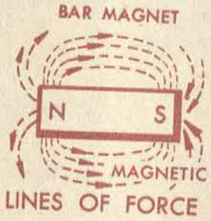
MATHEMATICS. A first-degree equation in one or more variables; an equation in which each term containing a variable is of the first degree.

Each of the following is a LINEAR EQUATION: $4x + 5 = 37$, $2x - 5y = 21$ *and* $7x + 4y - 5z = 10$.

linear programming \'lin-ē-ər 'prō-ˌgram-iŋ\

ENGINEERING and MATHEMATICS. A theory for determining the maximum value of a variable or of variables having a linear relation to each other. It is often used in computer programming.

LINEAR PROGRAMMING *is especially useful in the economic planning of large-scale industrial operations.*



line graph \'līn 'graf\

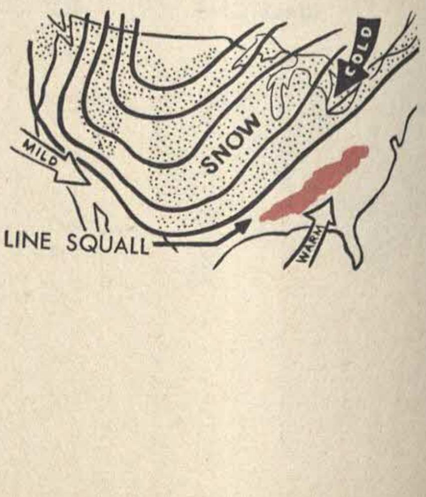
MATHEMATICS. A graph in which a statistical relation is represented by points in a rectangular coordinate system. The points are joined in order by straight line segments to show probable intermediate values of the dependent variable corresponding to intermediate values of the independent variable.

A LINE GRAPH *is often used to emphasize differences in numerical values.*

lines of force \'līnz əv 'fō(ə)rs\

EARTH SCIENCE and PHYSICS. In an electric field, lines that trace the path a positive charge would follow in going from the plus to the minus pole; also, in a magnetic field, the lines along which a small compass needle would align itself with reference to the north and south poles.

If not acted on by another field, a compass needle will align itself with one of the LINES OF FORCE *of the earth's magnetic field.*

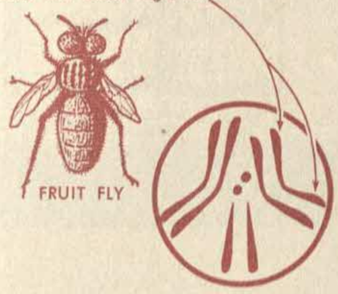


line squall \'līn 'skwȯl\

EARTH SCIENCE. A line of thunderstorms in advance of a fast-moving cold front.

A LINE SQUALL *has extremely-turbulent winds that sometimes develop into a tornado.*

Genes for black body color and vestigial wings located on this chromosome, so these two traits will occur together



LINKAGE

linkage \ˈliŋ-kij\ *n.*

1. BIOLOGY. A group of genes linked together in the same chromosome, resulting in an inheritance of characteristics, or traits, in groups. 2. CHEMISTRY. A covalent bond between two atoms. 3. ENGINEERING. A flexible joint between two rigid bars. 4. PHYSICS. The process by which one electric current gives rise to a second current through the phenomenon of induction.

A series of linked gene pairs in the same chromosome is known as a LINKAGE.

lipides \ˈlip-ˌīdz\ *n.*

CHEMISTRY. A group of organic compounds that have the characteristics of an oil, a fat or a wax and that are not soluble in water; also spelled lipid.

LIPIDES, *proteins and carbohydrates are the general classes of compounds that are contained in protoplasm.*

lipoid \ˈlip-ˌȯid\ *adj.*

BIOLOGY. Fatty; fatlike or resembling fat.

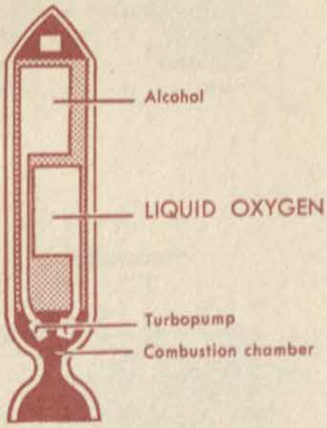
LIPOID *substances do not dissolve in water.*

liquid \ˈlik-wəd\ *n.*

CHEMISTRY. A substance that has a definite volume at a given temperature but not a definite shape, taking, instead, the shape of its container. A liquid is a substance that is neither gas nor solid.

LIQUID *is practically incompressible.*

LIQUID FUEL ROCKET



liquid air \ˈlik-wəd ˈa(ə)r\

CHEMISTRY. Air that has first been highly compressed and then has been cooled by expansion, forming a very cold, transparent liquid.

LIQUID AIR *does not have a definite boiling point.*

liquid measure \ˈlik-wəd ˈmezh-ər\

MATHEMATICS. A system used in measuring the volume of quantities of liquids.

The capacity of a bottle is usually expressed in LIQUID MEASURE.

liquid oxygen \ˈlik-wəd ˈäk-si-jən\

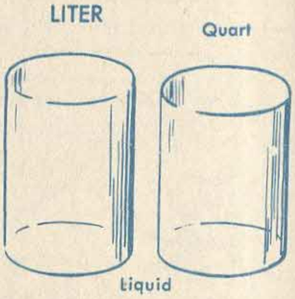
ASTRONAUTICS. A pale blue, transparent, mobile liquid, obtained by the compression of gaseous oxygen and used in liquid-oxygen explosives and as an oxidizer in rocket propellants; also called lox.

LIQUID OXYGEN *is highly explosive.*

liquid propellant \ˈlik-wəd prə-ˈpel-ənt\

ASTRONAUTICS. A rocket propellant in which the various components, such as the fuel and the oxidizer, are in the liquid state; also, referring to a type of rocket engine that uses a liquid propellant.

In 1926, Robert Goddard, an American scientist, launched the first successful rocket using a LIQUID PROPELLANT.



liter \ˈlēt-ər\ *n.*

MATHEMATICS. The volume occupied by 1 kilogram of pure water at 4° C. and 1 atmosphere of pressure. A liter is equal to 1,000 milliliters and approximately equal to 1,000 cubic centimeters.

A LITER *is slightly more than a liquid quart.*

literal \ˈlit-ə-rəl\ *adj.*

MATHEMATICS. Pertaining to any letter in an algebraic term; also, referring to an equation in which the coefficients of the variables or a constant term are represented by letters.

Two or more terms that have the same LITERAL *factor are similar.*

LITHIFICATION

lithification \ˌlith-ə-fi-ˈkā-shən\ *n.*

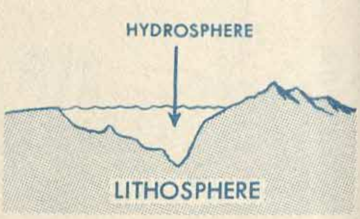
EARTH SCIENCE. The processes that change sedimentary deposits into rock.

LITHIFICATION *occurs when the weight of overlying sediments causes rock particles to be cemented together into a compact mass.*

lithosphere \ˈlith-ə-ˌsfi(ə)r\ *n.*

EARTH SCIENCE. The solid part, or crust, of the earth.

The LITHOSPHERE *includes the basins of lakes and oceans, as well as continents.*



litmus \ˈlit-məs\ *n.*

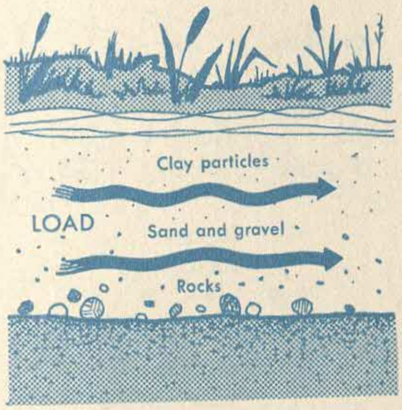
CHEMISTRY. A dye that is red in water solutions of acids and blue in water solutions of alkalies.

Strips of filter paper first soaked in LITMUS *and then dried are used as laboratory indicators of acid-base solutions.*

littoral \ˈlit-ə-rəl\ *adj.*

1. BIOLOGY. Pertaining to shore life, and, in fresh waters, confined to areas in which rooted vegetation occurs. 2. EARTH SCIENCE. Composed of material deposited near a shore.

Oil slicks caused by shipwrecks and underwater drilling often do extensive damage to LITTORAL *sea life.*



liver \'liv-ər\ *n.*

ANATOMY and ZOOLOGY. A glandular organ that secretes digestive fluids, such as bile, and, in vertebrates, destroys worn-out red corpuscles and stores vitamin A and glycogen.

In vertebrate animals, the LIVER *is the largest of all the glands in the body.*

load \'lōd\ *n.*

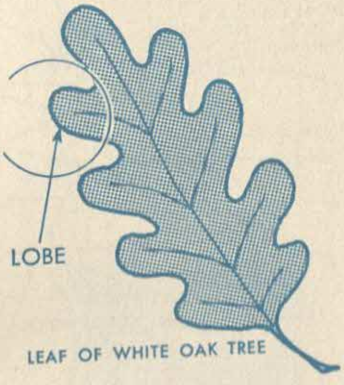
1. EARTH SCIENCE. Material, such as sand, gravel or clay, that is transported by a stream, a glacier or the wind. 2. PHYSICS. The total resistance or reactance in an electric circuit.

Part of a stream's LOAD *may be suspended in the water, and part of it may roll along the bottom.*

loam \'lōm\ *n.*

EARTH SCIENCE. Soil composed principally of sand and clay with varying amounts of silt and organic matter.

LOAM *is usually named according to the material that gives it special characteristics, such as sandy loam, silty loam or clay loam.*


LOBE
LEAF OF WHITE OAK TREE

lobe \'lōb\ *n.*

1. ANATOMY. A well-defined portion of an organ such as the brain or liver; also, the rounded lower part of the external ear. 2. BOTANY. A rounded division of a leaf.

The chief motor areas of the brain are located in the frontal LOBE *of the cerebral cortex.*

locus \'lō-kəs\ *n.*

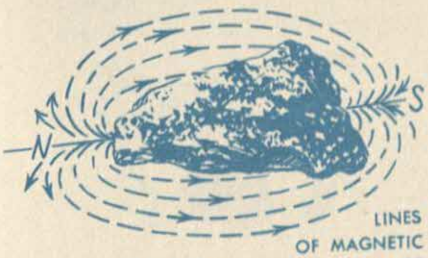
MATHEMATICS. The set of those points, and only those points, that satisfy a given condition or set of conditions.

The LOCUS *of an equation can be represented by a graph.*

lode \'lōd\ *n.*

EARTH SCIENCE. A mineral deposit formed in closely-spaced veins or rock fissures.

Sometimes, more than one metal can be mined from the same LODE.



LODESTONE

lodestone \'lōd-ˌstōn\ *n.*

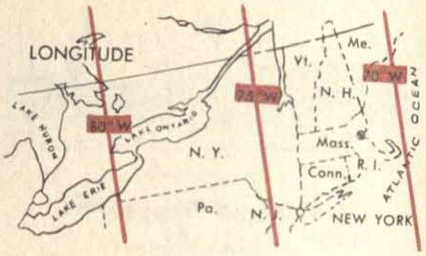
EARTH SCIENCE. A natural magnet composed of the mineral magnetite, Fe_3O_4.

A piece of LODESTONE *suspended on a thread will point to magnetic north.*

loess \ˈles\ *n.*

EARTH SCIENCE. A deposit of fine, loose material, mostly silt with some clay and sand particles. Such a deposit is usually yellow-brown in color.

Many geologists believe that LOESS *is material that has been transported and deposited by the wind.*



LONGITUDE

logarithm \ˈlȯg-ə-ˌrit͟h-əm\ *n.*

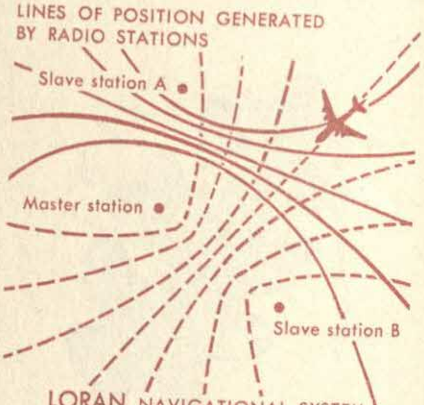
MATHEMATICS. The index of the power to which a fixed number, the base, must be raised in order to produce a given number.

Any number between 1 and 10 has a LOGARITHM *between 0 and 1.*

longitude \ˈlän-jə-ˌt(y)üd\ *n.*

EARTH SCIENCE. The angle formed at the earth's poles between a reference line, the Greenwich or prime meridian, and a meridian through any given point on the earth's surface. Longitude is calculated as a number of degrees east or west of the reference line.

Two places located exactly north and south of each other have the same LONGITUDE.



LORAN NAVIGATIONAL SYSTEM

loran \ˈlō(ə)r-ˌan\ *n.*

ENGINEERING. A navigational system in which pulsed signals from one or more pairs of radio stations of known position are used by a navigator to determine the position of his aircraft or ship.

LORAN *is an abbreviated term for* long range navigation.

low \ˈlō\ *n.*

EARTH SCIENCE. A region having an atmospheric pressure less than that of surrounding areas, usually less than normal pressure (14.7 pounds per square inch); see *cyclone.*

The weather associated with a LOW *is generally cloudy with rain or snow.*

low-frequency \ˈlō ˈfrē-kwən-sē\ *adj.*

PHYSICS. Pertaining to any frequency ranging from 30 to 300 kilocycles.

Amateur radio operators must use the LOW-FREQUENCY *range.*

lox \ˈläks\ *n.*

A term for liquid oxygen. See *liquid oxygen.*

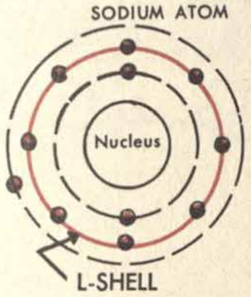
LSD

An abbreviation for lysergic acid diethylamide. See *lysergic acid diethylamide.*

L-shell \'el-ˌshel\ *n.*

CHEMISTRY and PHYSICS. One of the seven principal energy levels, identified by the letters K, L, M, N, O, P and Q, that electrons may occupy in an atom; the second principal energy level that electrons may occupy in the Bohr model for the atom.

There may be as many as eight electrons in the L-SHELL.



lumbar \'ləm-bər\ *adj.*

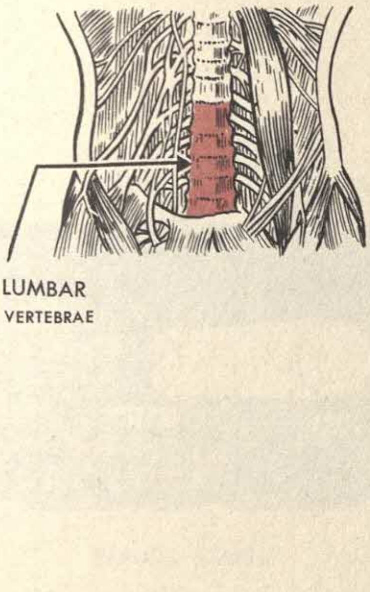
ANATOMY and ZOOLOGY. Pertaining to the lower part of the back or loin, as lumbar nerves, lumbar vertebrae or lumbar arteries.

In mammals, the largest vertebrae are those found in the LUMBAR *region.*

lumen \'lü-mən\ *n.*

1. PHYSICS. A unit for measuring intensity of light, equal to the illumination given off from a standard candle source and contained in a solid angle. 2. ANATOMY. The space inside a tubular organ, as in a blood vessel or a duct. 3. BIOLOGY. The space inside a cell.

One LUMEN *is equal to 0.0015 watt.*



luminescence \ˌlü-mə-'nes-ᵊn(t)s\ *n.*

PHYSICS. The emission of light from any substance that is not incandescent. The energy that excites the emitter may come from a chemical reaction (chemiluminescence), from mechanical action (triboluminescence) or from some other source.

The light produced in the abdomen of the firefly is an example of LUMINESCENCE.

luminosity \ˌlü-mə-'näs-ət-ē\ *n.*

ASTRONOMY. The intrinsic brightness of a star as compared to the brightness of the sun, the sun having been assigned a luminosity of one.

A giant star, such as Arcturus or Capella, has a LUMINOSITY *of approximately 100, which means it would appear to be 100 times brighter than the sun if it were the same distance from the earth as is the sun.*

lunar \'lü-nər\ *adj.*

ASTRONOMY. Relating to the moon or resembling the moon in shape.

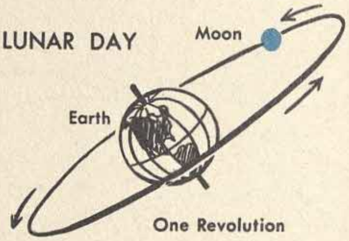
Modern astronomers disagree about the way LUNAR *craters were formed.*

LUNAR (CRATERS)

lunar day \'lü-nər 'dā\

ASTRONOMY. On the earth, the period of time (approximately 24 hours and 50 minutes) between two successive transits of the moon across an observer's meridian; also, on the moon, either the length of time it takes the moon to complete one rotation (about 28 earth days) or the length of time that there is sunlight on a given spot on the moon's surface (about 14 earth days).

On the earth, the LUNAR DAY *is shortest during the period of the harvest moon.*



LUNAR DAY

lunar eclipse \'lü-nər i-'klips\

ASTRONOMY. An eclipse of the moon caused by the earth's shadow falling on the moon.

A LUNAR ECLIPSE *occurs only when there is a full moon.*

lune \'lün\ *n.*

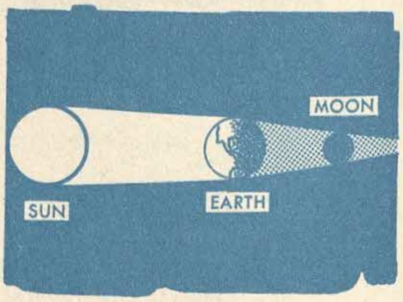
MATHEMATICS. A portion of a sphere created by, and lying between, two semicircles running from pole to pole, the semicircles being, in fact, halves of great circles of the sphere.

The line segment joining the vertices of a LUNE *is a diameter of the sphere.*

lung \'ləŋ\ *n.*

ANATOMY and ZOOLOGY. In man and higher vertebrates, one of two thin, elastic saclike organs that is a part of the respiratory system and that absorbs oxygen from the air and eliminates carbon dioxide.

In mammals, each LUNG *is covered by a double membrane called the pleura.*



LUNAR ECLIPSE

luster \'ləs-tər\ *n.*

EARTH SCIENCE. That special appearance of a mineral surface due to its light-reflecting characteristics, used as a means of identifying some minerals; more generally, the sheen, or the gloss, of an object as it reflects light.

A mineral having the shiny appearance of a metal is said to have metallic LUSTER.

lux \'ləks\ *n.*

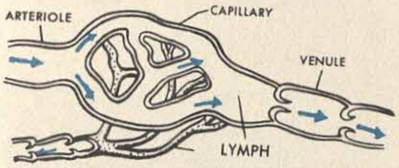
PHYSICS. A unit of illumination, or light intensity, equal to one lumen per square meter.

The LUX *is the unit of illumination derived from the mks system of units.*

lye \'lī\ *n.*

CHEMISTRY. NaOH (sodium hydroxide). A white, poisonous solid that dissolves readily in water, forming an alkaline solution that will neutralize acids.

The first step in treating skin that has been exposed to LYE *is to rinse it thoroughly with water.*



LYMPH

lymph \'lim(p)f\ *n.*

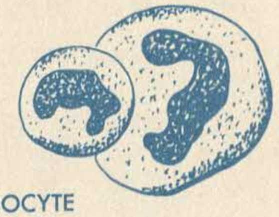
ANATOMY and PHYSIOLOGY. A colorless fluid that bathes the tissues, passes into lymphatic channels and ducts and is discharged into the blood by way of the thoracic duct. Lymph consists of a liquid, coagulable portion resembling blood plasma and contains numerous white blood cells.

The white blood cells in LYMPH *destroy harmful bacteria in the body.*

lymph node \'lim(p)f 'nōd\

ANATOMY. Any of the groups of glandlike bodies located along the paths of lymph vessels; also called lymph gland.

A LYMPH NODE *filters lymph and clears it of foreign particles, such as bacteria, carbon particles and malignant cells.*



LYMPHOCYTE

lymphocyte \'lim(p)-fə-ˌsīt\ *n.*

ANATOMY and PHYSIOLOGY. One of the three types of white cells formed by cell division in the lymph nodes.

A LYMPHOCYTE *is carried from a lymph node, through the lymph vessels and into the bloodstream.*

lysergic acid diethylamide \lə-'sər-jik 'as-əd ˌdi-ˌeth-əl-'am-ˌīd\

CHEMISTRY and MEDICINE. $C_{15}H_{15}N_2CON(C_2H_5)_2$. A crystalline solid obtained from ergot or synthesized in the laboratory. When taken as a drug, it causes severe hallucinations and symptoms resembling mental illness; also called LSD.

LYSERGIC ACID DIETHYLAMIDE *is the best-known of the psychedelic drugs.*

M

machine language \mə-'shēn 'laŋ-gwij\

ENGINEERING and MATHEMATICS. A system of coded symbols that can be interpreted by a digital computer.

The MACHINE LANGUAGE *fed to a common type of computer consists of various combinations of holes punched in a card.*

Mach number \'mäk 'nəm-bər\

PHYSICS. A number that expresses the ratio between the speed of a body and the speed of sound in the surrounding atmosphere.

Near the surface of the earth, a MACH NUMBER *of one is equivalent to a speed of about 750 miles per hour.*

MACKEREL SKY

mackerel sky \'mak-(ə-)rəl 'skī\

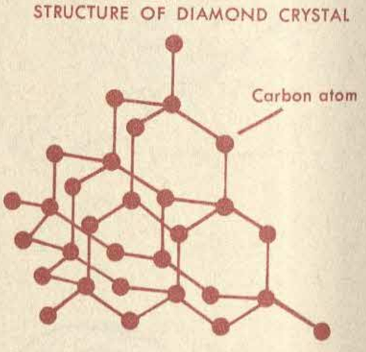
EARTH SCIENCE. A sky with cirrocumulus clouds in a pattern resembling the arrangement of scales on the sides of a mackerel.

A MACKEREL SKY *followed by lower, thicker clouds often indicates an approaching storm.*

macroclimate \'mak-(,)rō-,klī-mət\ *n.*

EARTH SCIENCE. The overall climate of a large geographic area, as opposed to the climate of a very small area.

Weather Bureau reports usually pertain to a MACROCLIMATE.

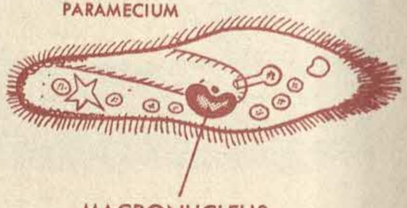


MACROMOLECULE

macromolecule \,mak-(,)rō-'mäl-i-,kyü(ə)l\ *n.*

CHEMISTRY. A large molecule held together by covalent bonds; also, a polymer of high molecular weight (about 40 million).

A diamond crystal is a MACROMOLECULE *because all its atoms are bonded together so that the whole crystal is one large molecule.*



MACRONUCLEUS

macronucleus \,mak-(,)rō-'n(y)ü-klē-əs\ *n.*

ZOOLOGY. A large nucleus found in certain protozoa that regulates the nutritional processes within the organism, as contrasted with the smaller micronucleus that functions during reproduction.

During the conjugation of two paramecia, the MACRONUCLEUS *in each will break up and disappear.*

macroscopic \\ˌmak-rə-ˈskäp-ik\\ *adj.*

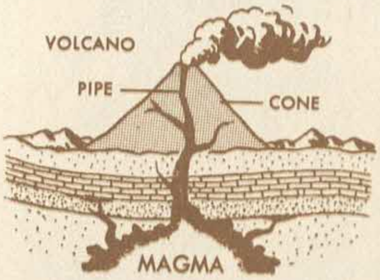
Large enough to be studied by the unaided eye, as contrasted with microscopic.

Certain parts of a frog are MACROSCOPIC, *while other parts can be studied only with a magnifying glass or microscope.*

Magellanic Clouds \\ˌmaj-ə-ˈlan-ik ˈklau̇dz\\

ASTRONOMY. Two irregular galaxies that are the nearest galaxies to the Milky Way system. They are visible to the naked eye as cloudlike, luminous patches.

Since the MAGELLANIC CLOUDS *are located within 25 degrees of the south celestial pole, they are not visible to observers north of the tropical zone.*



magma \\ˈmag-mə\\ *n.*

EARTH SCIENCE. A mass of molten rock materials and dissolved gases beneath the surface of the earth. Lava is magma that flows from volcanoes.

Igneous rocks are formed when MAGMA *cools and solidifies.*

magnesium \\mag-ˈnē-zē-əm\\ *n.*

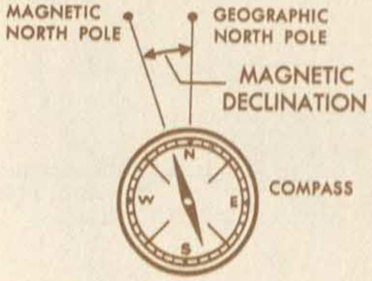
CHEMISTRY. A silvery, metallic element of low density. It resembles aluminum and is very active chemically. Symbol, Mg; atomic number, 12; atomic weight, 24.312.

Alloys of MAGNESIUM *and aluminum are used in aircraft construction because they are light but relatively strong.*

magnet \\ˈmag-nət\\ *n.*

PHYSICS. An object that will attract iron by a force other than gravitational, electrical or nuclear.

The force of a MAGNET *that attracts iron seems to come from its two poles.*



magnetic core \\mag-ˈnet-ik ˈkō(ə)r\\

ENGINEERING and MATHEMATICS. In a computer, an electromagnetic device used to store a binary digit.

The condition of a MAGNETIC CORE, *on or off, is checked by a sensing circuit within the computer.*

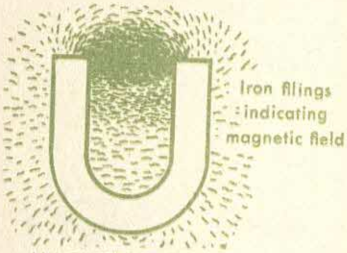
magnetic declination \\mag-ˈnet-ik ˌdek-lə-ˈnā-shən\\

EARTH SCIENCE. The acute angle formed at any point on the earth's surface by two lines: one from the point to the magnetic north pole and the other from the point to the geographic (true) north pole.

A navigator must correct any compass reading for MAGNETIC DECLINATION *to find his true direction.*

magnetic deviation \mag-'net-ik ˌdē-vē-'ā-shən\
EARTH SCIENCE and PHYSICS. The angle between magnetic north and north as indicated by a compass whose reading is affected by local interference or magnetism.

MAGNETIC DEVIATION *at a given place may be caused by the presence of large quantities of iron.*



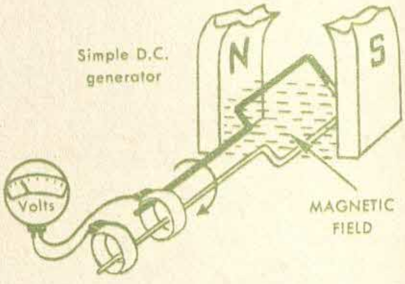
MAGNETIC FIELD

magnetic field \mag-'net-ik 'fēld\
PHYSICS. The space around a magnet or a conductor carrying electric current in which magnetic effects are observable.

The outline of a MAGNETIC FIELD *may be observed by sprinkling iron filings around a magnet.*

magnetic flux \mag-'net-ik 'fləks\
PHYSICS. Magnetic lines of force; commonly, the total number of magnetic lines of force passing through a given object placed in a magnetic field; also, the total amount of magnetic induction passing through a given plane surface.

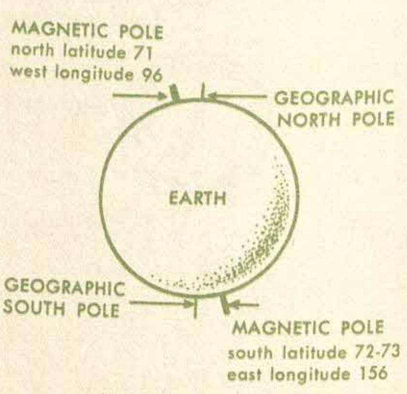
A keeper, an iron bar placed across the ends of a horseshoe magnet, concentrates the MAGNETIC FLUX *and prolongs the useful life of the magnet.*



MAGNETIC INDUCTION

magnetic induction \mag-'net-ik in-'dək-shən\
PHYSICS. The phenomenon by which voltage, or electromotive force, is produced in a conductor moving through a magnetic field; also, the phenomenon by which an unmagnetized piece of iron, or other material, becomes a magnet as a result of being placed in a magnetic field.

The voltage produced by electric generators is a result of MAGNETIC INDUCTION.



MAGNETIC POLES

magnetic poles \mag-'net-ik 'pōlz\
EARTH SCIENCE. The two points on the earth's surface where the needle of a dip compass will stand in a vertical position; the north and the south magnetic poles.

The earth's MAGNETIC POLES *do not coincide with its geographical poles.*

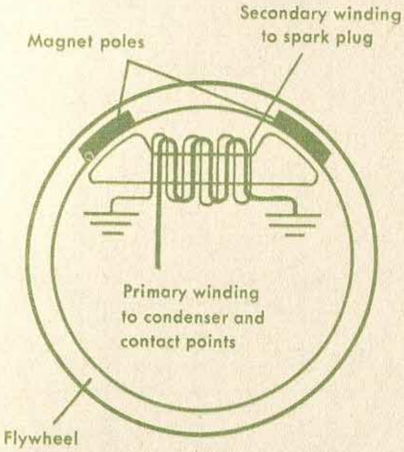
magnetic storms \mag-'net-ik 'stȯ(ə)rmz\
EARTH SCIENCE and PHYSICS. Irregular variations in the earth's magnetic field, lasting from several hours to several days and causing interruptions in electrical and radio communications.

MAGNETIC STORMS *are usually associated with the appearance of solar flares and sunspots.*

magnetism \'mag-nə-ˌtiz-əm\ *n.*

PHYSICS. That group of phenomena involving forces of both attraction and repulsion and associated with electrical charges moving in a conductor (as an electric current) or with spinning electrical charges (as in an atom); in particular, events that occur in a field of influence caused by a magnet.

Scientists have not yet explained the exact physical nature of MAGNETISM.


Secondary winding to spark plug
Magnet poles
Primary winding to condenser and contact points
Flywheel

MAGNETO
(ROTARY)

magneto \mag-'nēt-(ˌ)-ō\ *n.*

ENGINEERING. A device for producing the high-voltage alternating current that fires the spark plugs of some internal-combustion engines.

A gasoline-powered lawnmower utilizes a MAGNETO *that is attached to the flywheel.*

magnetron \'mag-nə-ˌträn\ *n.*

PHYSICS. A device used for generating electromagnetic waves of microwave frequency. It consists of a vacuum tube in which a flow of electrons from cathode to anode is controlled by an externally-applied magnet.

A MAGNETRON *is used to generate the radio waves of very high frequency that are used in radar, which are beyond the capacity of ordinary tubes.*

MAGNIFICATION

magnification \ˌmag-nə-fə-'kā-shən\ *n.*

PHYSICS. The apparent enlargement of an object when viewed through a lens or a system of lenses.

Very fine print is hard to read without MAGNIFICATION.

magnitude \'mag-nə-ˌt(y)üd\ *n.*

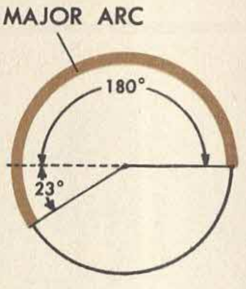
1. ASTRONOMY. A comparative number used to indicate the brightness of a star, planet or other celestial body. 2. MATHEMATICS. Size, greatness or extent of a quantity relative to some unit of measure; also, that property of a measurable quantity that may be represented as a line segment of definite length.

Apparent MAGNITUDE *refers to the brightness of a star as we see it, while absolute magnitude indicates the star's intrinsic, or actual, brightness.*

main-sequence stars \'mān 'sē-kwən(t)s 'stärz\

ASTRONOMY. The stars that are included in a broad band extending from the upper left to the lower right on a spectrum-luminosity (Hertzsprung-Russell) diagram. Included are our sun and most other stars, but not the giants, the supergiants and the dwarfs.

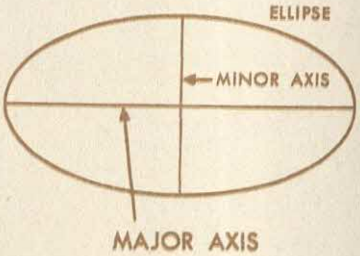
A star's position on the spectrum-luminosity diagram with respect to the MAIN-SEQUENCE STARS *is believed to indicate its stage of evolution.*



major arc \'mā-jər 'ärk\

MATHEMATICS. An arc, or portion of a circle, that is greater than a semicircle.

A central angle that intercepts a MAJOR ARC *is greater than a straight angle.*



major axis \'mā-jər 'ak-səs\

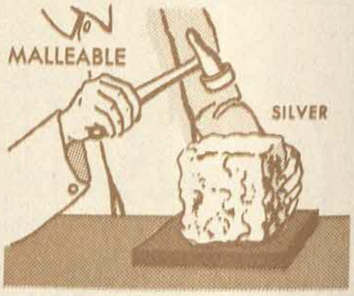
MATHEMATICS. The longer of the two axes of symmetry of an ellipse; also, the longest of the diameters of an ellipse.

The length of the MAJOR AXIS *of an ellipse is equal to the sum of the distances from any point on the ellipse to the two foci of the ellipse.*

male \'māl\ *adj.*

1. ANATOMY and ZOOLOGY. Referring to that sex which produces sperm that unite with the egg, or ovum, of a female to produce a new animal; also, referring to the characteristics of that sex. 2. BOTANY. Pertaining to a plant, or to organs of a plant, that fertilizes the pistillate plant of its own variety; staminate; see *stamen.*

The reproductive cells of a MALE *animal are usually adapted for movement, but the egg cells of the female ordinarily do not have this ability.*



malleable \'mal-ē-ə-bəl\ *adj.*

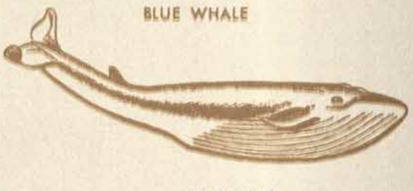
CHEMISTRY and PHYSICS. Capable of being formed into a shape by hammering, pressing or rolling.

Cast iron may be made MALLEABLE *by maintaining it at a temperature of 800° C. for several days and then cooling it slowly.*

maltose \'mȯl-ˌtōs\ *n.*

CHEMISTRY. $C_{12}H_{22}O_{11}$. A sugar formed by the partial decomposition of starch and promoted by the presence of a specific enzyme; a disaccharide.

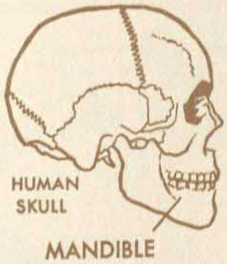
When barley sprouts, some of its starch is converted to MALTOSE.



mammal \'mam-əl\ *n.*

ZOOLOGY. One of the class of vertebrates (Mammalia) including man and the warm-blooded quadrupeds that grow hair and feed their young on milk.

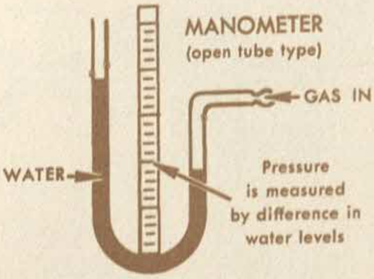
Although it has some fishlike characteristics, the whale is a MAMMAL.



mandible \'man-də-bəl\ *n.*

1. ANATOMY. A jaw, especially the lower jaw. 2. ZOOLOGY. A similar structure in mammals; also, either part of the beak of a bird; also, a biting part of the mouth of arthropods.

The MANDIBLE *in man is somewhat V-shaped and contains the set of lower teeth.*



manometer \mə-'näm-ət-ər\ *n.*

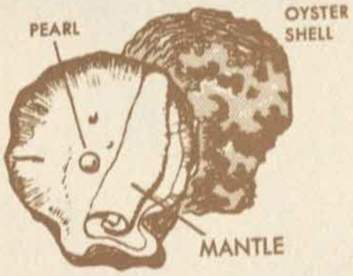
1. PHYSICS. A device used to measure the pressure in fluids; a pressure gauge. 2. MEDICINE and PHYSIOLOGY. An instrument used to measure blood pressure in arteries by means of an inflated pressure cuff that is connected to it.

A MANOMETER *is often made in the form of a U-shaped glass tube.*

mantissa \man-'tis-ə\ *n.*

MATHEMATICS. The part of a logarithm that is represented by a decimal fraction or that appears to the right of the decimal point.

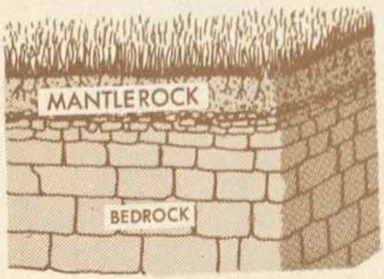
The MANTISSA *always has a value ranging from zero to one.*



mantle \'mant-ᵊl\ *n.*

1. ZOOLOGY. The membranous flaps or folds in the body wall of a mollusk or similar organism, containing glands that secrete a shell-forming fluid; also, the soft, outer wall of a tunicate or barnacle; also, the back and folded wings of a bird. 2. ANATOMY. The cortex of the cerebrum. 3. EARTH SCIENCE. The part of the earth between the crust and the core that extends to a depth of about 1,800 miles and is believed to be composed of ferromagnesian minerals.

A pearl is formed around such particles as sand grains that have become lodged between the MANTLE *and the shell of certain mollusks.*



mantlerock \'mant-ᵊl-ˌräk\ *n.*

EARTH SCIENCE. The layer of loose rock fragments, earth and soil that covers land areas; the regolith.

MANTLEROCK *rests on top of bedrock.*

mapping \'map-iŋ \n.

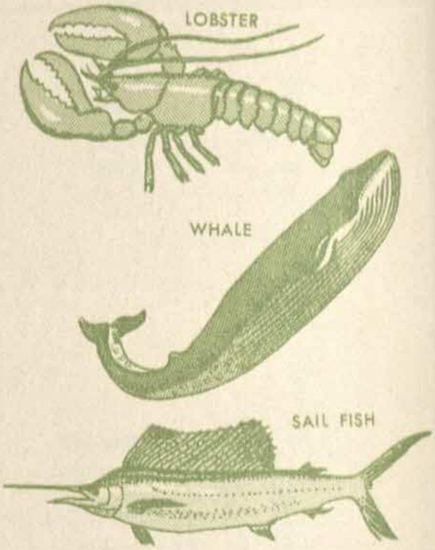
MATHEMATICS. A correspondence, or relation, between two sets that associates, or matches, with each element of the first set a unique element of the second set.

The concept of MAPPING *is closely related to the concept of function.*

marble \'mär-bəl\ *n.*

EARTH SCIENCE. A metamorphic rock consisting of calcite, $CaCO_3$. It is an altered limestone or dolomite that takes a fine polish.

The principal uses of MARBLE *are as a building stone and for statues.*



MARINE

marine \mə-'rēn\ *adj.*

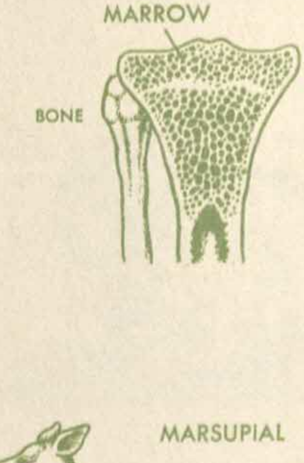
Pertaining to, or living in, a sea, an ocean or another body of salt water.

Whales, lobsters and sailfish are all MARINE *animals.*

marrow \'mar-(ˌ)ō\ *n.*

ANATOMY and ZOOLOGY. The soft, fatty tissue found in the cavities of many bones.

Red blood cells are formed in the red MARROW *of the bones.*



marsh \'märsh\ *n.*

EARTH SCIENCE. A tract of relatively-low, flat land that is partly or completely covered with standing water and thick vegetation; a swamp; a bog.

A MARSH *may be the result of sediment filling a lake.*

marsh gas \'märsh 'gas\

CHEMISTRY. CH_4. A burnable gas, methane, frequently formed in swamps. It is formed by the underwater decay of organic matter.

If MARSH GAS *ignites in a swamp, it may be seen on moonless nights as a dim flicker of light that has come to be known as "swamp fire" or "will-o'-the-wisp."*

MARSUPIAL

marsupial \mär-'sü-pē-əl\ *n.*

ZOOLOGY. A mammal, the female of which has a pouch on the abdomen in which the young are carried and nourished, such as an opossum or kangaroo.

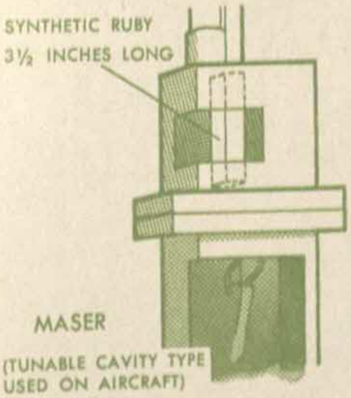
The young of a MARSUPIAL *spends its early infancy in the mother's pouch.*

maser \'mā-zər\ *n.*
PHYSICS. An electronic device that produces microwaves in a very narrow frequency range.

MASER *comes from the first letters in the expression "microwave amplification by stimulated emission of radiation."*

mass \'mas\ *n.*
PHYSICS. The quantitative measure of an object's property to resist changes in its motion; also, the amount of matter in an object, measured in units, such as the gram and kilogram.

The weight of an object may be different if measured on different planets, but the object's MASS *is the same everywhere.*

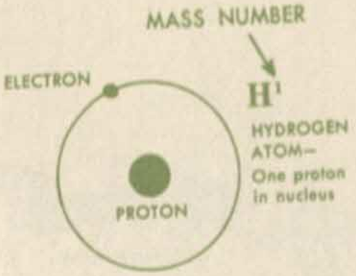


mass defect \'mas 'dē-ˌfekt\
PHYSICS. The difference between the total individual masses of the protons and neutrons in the nucleus of an atom and the mass of the nucleus as a whole. The latter mass is smaller, and the apparent loss of mass occurs as binding energy that contributes to holding the nucleus together.

MASS DEFECT *is frequently given as evidence for the equality of mass and energy.*

mass-energy equation \'mas 'en-ər-jē i-'kwā-zhən\
PHYSICS. The mathematical expression describing the fact that mass, or matter, can be changed into energy or energy into mass: $E = mc^2$, in which E equals energy in joules, m equals mass in kilograms and c equals the velocity of light in meters per second.

The MASS-ENERGY EQUATION *is frequently referred to as Einstein's equation.*



mass number \'mas 'nəm-bər\
PHYSICS. The total number of protons and neutrons in the nucleus of an atom. Mass number is nearly the same as atomic weight.

The MASS NUMBER *of a radioisotope of carbon is 14, but that of the common nonradioactive isotope of carbon is 12.*

mass ratio \'mas 'rā-(ˌ)shō\
ASTRONAUTICS. The ratio of a rocket's total mass to its mass after all the fuel has been used.

The ejection of the burned-out stage of a multistage rocket increases the MASS RATIO *of the remaining stages of the rocket, thus making possible increased speeds.*

mass spectograph \'mas 'spek-t(r)ə-,graf\

PHYSICS. A device that separates mixtures of electrically-charged atoms or molecules. In operation, moving, charged particles are deflected by a magnetic field, the amount of deflection depending on the speed, mass and charge of the particles. A record of the separated particles is made photographically.

The MASS SPECTROGRAPH *has been used in discovering isotopes of many elements.*

mass unit \'mas 'yü-nət\

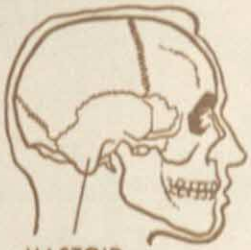
PHYSICS. A standard unit for expressing mass and a basis for comparing the mass of objects.

The MASS UNIT *in the mks system is the kilogram, in the cgs system it is the gram and in the fps system it is the slug.*

mastoid \'mas-,tȯid\ *n.*

ANATOMY. A part of the temporal bone, shaped like a nipple and located behind the ear.

The MASTOID *contains small chambers, known as air cells, that sometimes become infected.*



MASTOID

maternal \mə-'tərn-ᵊl\ *adj.*

ANATOMY and ZOOLOGY. Of, like or characteristic of a mother; also, inherited, derived or received from a mother.

Many female animals have a MATERNAL *instinct that causes them to care for their offspring.*

MATERNAL

POLAR BEAR AND CUB

mathematician \,math-(ə-)mə-'tish-ən\ *n.*

MATHEMATICS. One who is well versed in all branches of mathematics and who is an expert in one or a number of branches of advanced mathematics.

A MATHEMATICIAN *usually devotes a great deal of time to research work in his special field of mathematical interest.*

mathematics \,math-ə-'mat-iks\ *n.*

The science that includes both the practical and the theoretical study of form, space and number.

MATHEMATICS *includes such branches of study as arithmetic, algebra, geometry and calculus.*

MATRIX

matrix \'mā-triks\ *n.*

1. EARTH SCIENCE. Fine-grained minerals or rock particles that fill the spaces between larger particles, crystals or fossils; the groundmass. 2. BIOLOGY. The material between the cells of a tissue. 3. ANATOMY. The uterus; also, a place of origin and

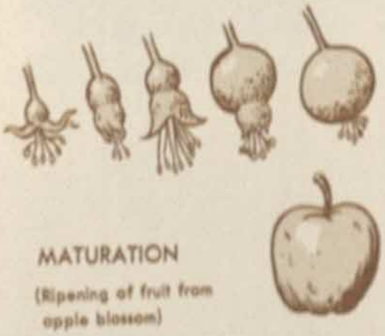
growth, as the dermis of the fingernail and toenail. 4. MATHEMATICS. A rectangular arrangement of terms, called elements, that is particularly useful in the study of systems of linear equations.

Mineral ores often consist of a MATRIX *of rock in which the mineral is embedded.*

matter \'mat-ər\ *n.*

PHYSICS. Anything that has the property of inertia and that can be located in space; also, anything that has mass and occupies space.

Because the mass of an electron is less than that of a neutron, it is considered to be a smaller particle of MATTER.



MATURATION

(Ripening of fruit from apple blossom)

maturation \ˌmach-ə-'rā-shən\ *n.*

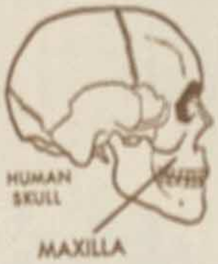
BIOLOGY. Ripening; also, completion of germ cell development, consisting of the reduction of chromatin; also, in meiosis, reduction of chromosomes from diploid to haploid number; also, the development of adult characteristics.

The MATURATION *process in animals involves the formation of spermatozoa and eggs, and in plants the formation of megaspores and microspores.*

maxilla \mak-'sil-ə\ *n.*

1. ANATOMY. One of the two upper jawbones, each of which contains an air space known as a maxillary sinus; also, the superior maxilla as contrasted with the inferior maxilla, or mandible. 2. ZOOLOGY. An appendage of most arthropods; also, the upper jaw of an animal, or part of the upper jaw behind the premaxilla.

The upper teeth develop in the MAXILLA.



maxilliped \mak-'sil-ə-ˌped\ *n.*

ZOOLOGY. An appendage in one, two or three pairs posterior to the maxillae in arthropods.

The MAXILLIPED *of a crayfish functions as an organ of touch, taste and ingestion.*

maxwell \'mak-ˌswel\ *n.*

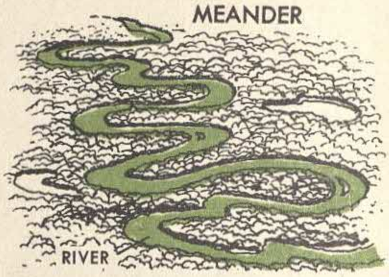
PHYSICS. The unit of magnetic flux in the centimeter-gram-second system that represents one line of magnetic flux.

The MAXWELL *was named for James Clerk Maxwell, a Scottish physicist who predicted radio waves.*

mean \'mēn\ *n.*

MATHEMATICS. An intermediate value that is the arithmetic average of a set of numbers determined by dividing the sum of the numbers by the cardinal number of the set; also, the n^{th} root of the product of a set of n numbers.

The arithmetic MEAN *of 5, 7, 32 and 44 is the sum of these figures divided by 4, or 22.*



meander \mē-'an-dər\ *n.*

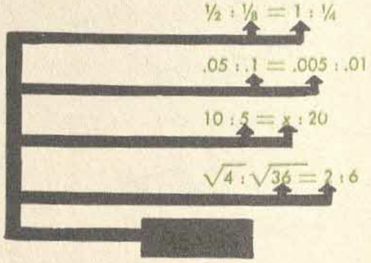
EARTH SCIENCE. A looping bend in a stream or river, usually occurring in a series and typical of a stream flowing in a flat, wide valley.

A MEANDER *may form when a stream is diverted by an obstruction in its channel.*

means \'mēnz\ *n.*

MATHEMATICS. The second and the third terms of a proportion. In the proportion 4:6 = 2:3, the numbers 6 and 2 are the means.

In a proportion, the product of the MEANS *is equal to the product of the extremes.*



mean solar time \'mēn 'sō-lər 'tīm\

ASTRONOMY. Time based on the average length of a solar day during the course of a year. The use of mean solar time is necessary because the time intervals between the sun's crossing of the meridian at a given location are not the same each day.

Because our clocks are set according to MEAN SOLAR TIME, *they do not agree with sundial time during most of the year.*

measure \'mezh-ər\

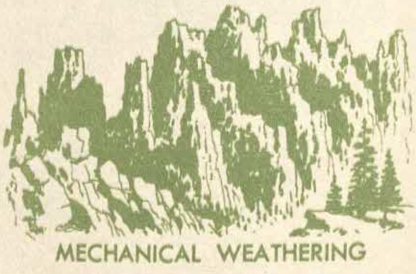
MATHEMATICS (V.). To determine the number of times a fixed standard unit or derived unit is contained in a given quantity. (N.). The size or extent of a given quantity as determined by comparison with a fixed standard unit or derived unit.

A protractor is often used to MEASURE *angles.*

mechanical engineering \mi-'kan-i-kəl ˌen-jə-'ni(ə)r-iŋ\

ENGINEERING. The practical application of a knowledge of machines and power.

MECHANICAL ENGINEERING *is required to produce an automobile.*



MECHANICAL WEATHERING

mechanical weathering \mi-'kan-i-kəl 'weṯẖ-(ə-)riŋ\

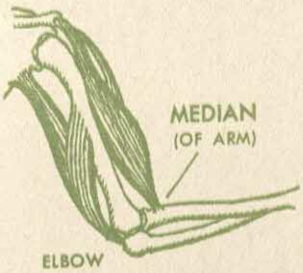
EARTH SCIENCE. The process by which rocks are broken down into smaller and smaller fragments as a result of physical forces, such as expansion and contraction caused by temperature changes, frost action or abrasion by water, ice or wind.

MECHANICAL WEATHERING *does not affect the chemical composition of rocks.*

mechanics \mi-'kan-iks\ *n.*

PHYSICS. A branch of physical science that is concerned with energy and the action of forces; sometimes called dynamics.

Pneumatics is the phase of MECHANICS *that deals with gases.*



medial \'mēd-ē-əl\ *adj.*

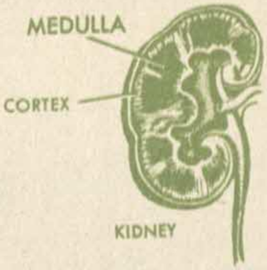
ANATOMY. Referring to a plane that would divide the body lengthwise into approximately equal halves; also, referring to the middle or something near the middle.

The spinal column lies along the MEDIAL *plane behind the body cavity.*

median \'mēd-ē-ən\ *n.*

1. ANATOMY. A position or placement in the middle of the body, or in the middle of a part of the body. 2. MATHEMATICS. The middle value or number in an ordered set of data if the cardinal number of the set is odd. If the set is even, it is the average of the two middle values.

The elbow is in the MEDIAN *of the arm.*



medicine \'med-ə-sən\ *n.*

The art and science dealing with the maintenance of health and the prevention and treatment of disease, sometimes including surgery and obstetrics; also, a preparation used to treat a disease.

Penicillin is a modern MEDICINE *that is effective in the treatment of a number of infections.*

medium \'mēd-ē-əm\ *n.*

1. BIOLOGY and MEDICINE. A mixture, such as nutrient agar or beef extract, in which microorganisms are cultivated for study or research; see *culture medium.* 2. The surroundings or substance in which a given process, event or phenomenon takes place.

Yeast can be raised in a MEDIUM *consisting of sugar and water.*

medulla \mə-'dəl-ə\ *n.*

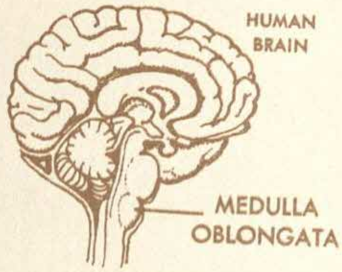
ANATOMY. The central part of an organ, as contrasted with the cortex or outer part of the organ; also, the marrow.

The MEDULLA *of the adrenal gland secretes the hormone epinephrine.*

medulla oblongata \mə-'dəl-ə ˌäb-ˌlȯŋ-'gät-ə\

ANATOMY. The lower part of the brain that is an extension of the spinal cord.

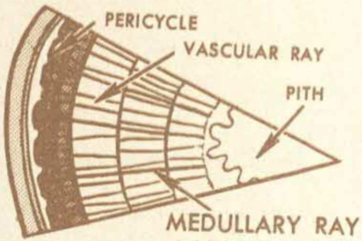
The MEDULLA OBLONGATA *contains the nerve centers that regulate the rate of respiration, the heartbeat, swallowing and other reflex actions.*



medullary ray \'med-ᵊl-ˌer-ē 'rā\

1. BOTANY. A strand of tissue extending from the pith and separating the vascular bundles in the stems of certain plants. 2. ANATOMY. An extension of a kidney tubule into the cortex.

In a dicotyledonous plant, the MEDULLARY RAY *extends between the pith and the pericycle.*



(of 3-year-old stem)

megacycle \'meg-ə-ˌsī-kəl\ *n.*

PHYSICS. One million cycles. Megacycle is frequently used to mean one million cycles per second; *abbr.* mc or mc/s.

The broadcast bands of FM radio stations are centered on a frequency that is some multiple of one MEGACYCLE.

megascopic \ˌmeg-ə-'skäp-ik\ *adj.*

Visible to the unaided eye; macroscopic.

The word MEGASCOPIC *is used especially to specify those features of rocks that can be observed without the aid of magnifying equipment.*

megaspore \'meg-ə-ˌspō(ə)r\ *n.*

BOTANY. A spore that develops into the female gametophyte; also, the sexual generation of a plant.

Upon germination, each MEGASPORE *will give rise to a female gametophyte.*

megaton \'meg-ə-ˌtən\ *n.*

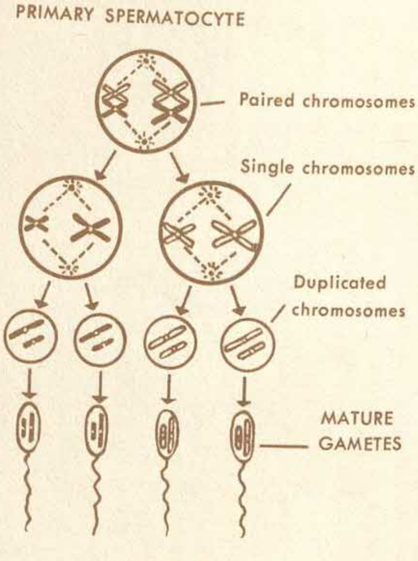
PHYSICS. One million tons; also, the amount of energy that would be released if one million tons of TNT were exploded.

The explosive energy of a hydrogen bomb may be expressed as some multiple of one MEGATON.

meiosis \mī-'ō-səs\ *n.*

BIOLOGY. Nuclear divisions of germ cells giving rise to gametes (spermatozoa and eggs) in animals and spores (microspores and megaspores) in the higher plants.

In MEIOSIS, *germ cell chromosomes are reduced from diploid to haploid number at maturation.*

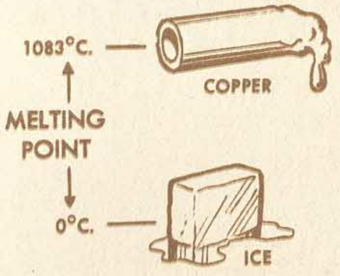


MEIOSIS

melting point \'melt-iŋ 'pȯint\

CHEMISTRY and PHYSICS. The temperature at which a given solid changes into a liquid. The temperature is different for different substances.

A true compound has a definite MELTING POINT, *while materials such as glass and butter do not.*



member \'mem-bər\ *n.*

MATHEMATICS. Either of the two parts of an equation separated by the sign of equality, the parts being denoted as the left member and the right member; also, an element or an object that belongs to a set of objects.

The left MEMBER *of the equation* $5x + 3 = 2y - 6$ *is* $5x + 3$.

membrane \'mem-ˌbrān\ *n.*

ANATOMY. A thin sheet of tissue that covers separate organs or lines such cavities as the thorax and the abdomen.

The peritoneum is a MEMBRANE *that lines the abdominal cavity and covers most of the organs within the abdomen.*

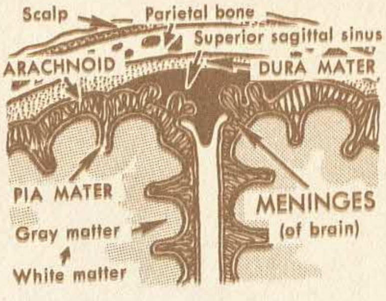
Mendeleev's law \ˌmen-dᵊl-'ā-əfs 'lȯ\

Mendeleev's periodic law. See *periodic law.*

Mendel's laws \'men-dᵊlz 'lȯz\

BIOLOGY. The three fundamental principles of inheritance: the law of unit characters, the law of dominance and the law of segregation. The law of unit characters states that inherited characteristics are determined and transmitted by individual but paired factors. The law of dominance states that when two contrasting factors occur in an organism, one suppresses the expression of the other. The law of segregation states that factors are separated and redistributed by chance during sexual reproduction.

Although MENDEL'S LAWS *are basic to modern genetics, exceptions such as multiple alleles, provisional dominance and crossing-over are known to occur.*



meninges \mə-'nin-(ˌ)jēz\ *n.*

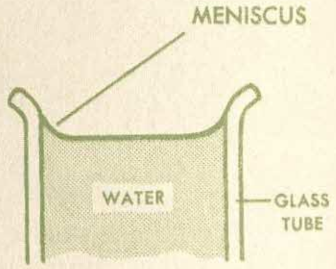
ANATOMY. The three membranes, or layers of tissue, that cover the brain and the spinal cord: dura mater, arachnoid tissue and pia mater.

Spinal meningitis is an inflammation of the MENINGES *caused by bacterial infection.*

meniscus \mə-'nis-kəs\ *n.*

1. PHYSICS. The curved upper surface of a liquid in a container. 2. ANATOMY. A disk of cartilage, occurring at the ends of the bones in certain joints of the body.

Water in a partly-filled glass tube forms a MENISCUS *that is concave upward.*



mensuration \ˌmen(t)-sə-'rā-shən\ *n.*

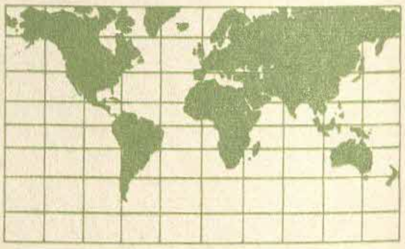
MATHEMATICS. The phase of mathematics that deals with the measurement of geometric magnitudes, such as lengths of lines, measures of angles, areas of surfaces and volumes of solids, by direct or indirect methods.

MENSURATION *is not generally considered to be a separate branch of mathematics, but is often thought of as a part of geometry, trigonometry and calculus.*

Mercator map projection \(ˌ)mər-'kāt-ər 'map prə-'jek-shən\

EARTH SCIENCE. A map of the earth drawn by projecting the surface features onto the surface of a cylinder tangent to the earth at the equator. When the cylinder is unrolled, the meridians appear as parallel, equidistant, straight lines that cross the lines of latitude at right angles. The lines of latitude are also parallel and straight but are spaced farther apart with increasing latitude.

The MERCATOR MAP PROJECTION *results in an extreme increase in apparent size of areas at latitudes greater than 60 degrees.*



MERCATOR MAP PROJECTION

mercurial barometer \(ˌ)mər-'kyůr-ē-əl bə-'räm-ət-ər\

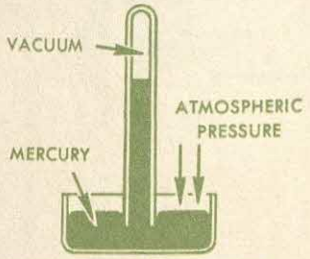
PHYSICS. An instrument that measures atmospheric pressure. Frequently, it is made of a glass tube about three feet long that is closed at one end, filled with mercury and placed, open end down, in a dish of mercury.

A MERCURIAL BAROMETER *is usually the standard with which other types of barometers are compared.*

mercury \'mər-kyə-rē\ *n.*

CHEMISTRY. A metallic element that is liquid at ordinary temperatures and has a density of 13.546 grams per cubic centimeter; also called quicksilver. Symbol, Hg; atomic number, 80; atomic weight, 200.59.

Iron, because of its lower density, floats in MERCURY.



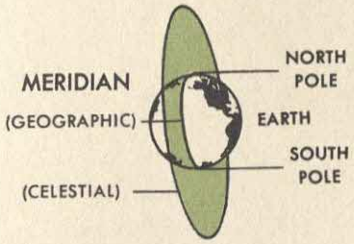
MERCURIAL BAROMETER

meridian \mə-'rid-ē-ən\ *n.*

1. EARTH SCIENCE. An imaginary line that passes from the North to the South Pole through any given place on the earth's sur-

face; also, one of the standard lines of longitude. 2. ASTRONOMY. A great circle on the celestial sphere that passes through the north and south celestial poles and an observer's zenith.

Local noon is defined as the time at which the sun crosses the MERIDIAN *at a particular location.*



meristem \\'mer-ə-ˌstem\\ *n.*
BOTANY. A group of cells capable of repeated division, such as those located at the growing tips of plant roots and branches and in the cambium layer; also, undifferentiated tissue capable of differentiating into specialized tissue.

Rapid growth in root length is largely the result of elongation of cells back of the MERISTEM.

mesa \\'mā-sə\\ *n.*
EARTH SCIENCE. A large, flat-topped, elevated land area with steep cliffs on one or more sides; a tableland.

A MESA *is usually made up of nearly-horizontal rock beds.*

MESA

mesencephalon \\ˌmez-ˌen-'sef-ə-ˌlän\\ *n.*
ANATOMY and PHYSIOLOGY. The midbrain, a centrally-located segment of the brain that includes the cerebral peduncles, the cerebral aqueduct and the red nucleus.

The MESENCEPHALON *is the short upper part of the brain stem that divides into two branches, leading to the two halves of the cerebrum.*

mesentery \\'mes-ᵊn-ˌter-ē\\ *n.*
ANATOMY and ZOOLOGY. A fold in the tissue lining the abdominal cavity of vertebrates, connecting the digestive tube to the back part of the abdominal wall.

Blood vessels and nerves pass through the MESENTERY *to the organs of the body.*

mesoderm \\'mez-ə-ˌdərm\\ *n.*
ZOOLOGY. The middle layer of cells in an animal embryo; the layer lying between the ectoderm and the endoderm.

The bones, muscles, blood vessels, reproductive organs and coverings of body cavities are formed from the cells of the MESODERM.